Base Resistant Polymethylene Type Fluoro-elastomers for Oil & Gas

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ABSTRACT

FEPM class polymers have solved many problems for the oil & gas industry for the past five decades, particularly in hot aqueous and other corrosive environments requiring corrosion inhibitors with their subsequent high pH. While most of the FEPM grades have been available during this time frame, one has received little publicity in spite of its unique performance characteristics. In more recent years, FKM Types 4 & 5 have been introduced to expand available "base resistant" options for colder operating temperatures.

Subsequent to the collapse in oil prices over the past decade, the current economics of the oil & gas industry has been demanding more performance for less cost. Non-metallic materials have been no exception to this industry demand.

This study examines the fluoroelastomers positioned as "base resistant" in the market place. Since there is limited data publicly available on these materials, this study offers new data that might help the tool engineer or field operator realize a better value proposition in elastomeric sealing materials for hot, high pH operating environments.

INTRODUCTION

Fluoroelastomers established their place in the oil and gas industry many decades ago. FKM elastomers, specifically Type 1, made their debut in the late 1950's as a sealing material that not only resisted hydrocarbons but proved capable of operating at temperatures upwards of 200C. Various FKM elastomer grades were introduced over the following years that represented different mixtures and ratios of vinylidene fluoride, hexafluoropropylene, and tetrafluoroethylene (aka FKM Type 1 and Type 2) to enhance chemical resistance and physical properties. Soon thereafter, perfluoromethyl vinyl ether was being incorporated as a monomer to improve cold temperature performance (aka FKM Type 3). The FKM class of elastomers share a common thread: they all include vinylidene fluoride as a cure site monomer which allows the use of an amine to initiate a cure site. As the production of sour hydrocarbons increased over the years, so did the need for increasing the use of amine based corrosion inhibitors. As a consequence, FKM sealing materials increasingly fared poorly.

A decade after the introduction of FKM fluoro-rubber, fluoro-rubber grades that did not contain vinylidene fluoride appeared. DuPont introduced the first commercially available fully fluorinated elastomer known as Kalrez® in the late 1960's. In the mid 1970's, Asahi Glass introduced a tetrafluoroethylene & propylene copolymer known as Aflas®. These milestone introductions constituted the first fluoro-elastomers that could be used to contain high pH solutions without degradation. In subsequent years, the ASTM D1418[1] standard for rubber nomenclature evolved to reflect these distinctions as FKM, FFKM, and FEPM class rubber.

One complaint concerning the tetrafluoroethylene & propylene copolymer is the material's rigidity near the freezing point (O°C). The need for an elastomer that can handle high pH solutions at colder temperatures preceded the introduction of Type 4 and Type 5 FKM's. The few materials classified as Type 4 and Type 5 currently claim improved base resistance. While these materials are not technically FEPM class elastomers, they will be examined herein alongside the two prevailing FEPM class materials since they have been positioned in the market as "base resistant".

Fully fluorinated rubber solved the requirement of broad spectrum chemical resistance and thermal stability in the 1970's. However, this problem solver is very expensive relative to the field of other fluoro rubbers. From a raw material perspective, it is about one hundred (100) times more expensive than FKM's. After DuPont introduced its Kalrez (FFKM) material, it introduced an elastomer known as Viton® ETP comprised of tetrafluoroethylene, ethylene, perfluoromethyl

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[1] ASTM Standard D 1418 – 10a, "Standard Practice for Rubber and Rubber Latices-Nomenclature", section 9, *Annu. Book ASTM Stand.* 09.01, (2011).

vinyl ether, and a cure site monomer. While ETP costs roughly ten (10) times more than an FKM, it also costs one-tenth the price of an FFKM. Viton ETP will be examined herein as well.

In the current economic environment, field operators remain under pressure to control costs at every level of the supply chain. This paper's objective is to provide comparative data and explanation of some unique reportedly "base resistant" fluoroelastomers and where they might satisfactorily perform at considerable discounts to one another.

Base Resistant Fluoroelastomers

ASTM D1418-10a has established nomenclature for the designation of rubber. This paper focuses on polymethylene type ("M" class) fluororubber. More specifically, the FKM Type 4 & Type 5 ("base resistant") and FEPM class elastomers are examined. Although FFKM elastomers are base resistant, they have been omitted from this study. ASTM D1418-10a defines the fluorinated polymers of interest as follows:

> "FEPM – A fluoro rubber of the polymethylene type only containing one or more of the monomeric alkyl, perfluoroalkyl, and/or perfluoroalkoxy groups, with or without a cure site monomer…"[2].
> "FKM - Fluoro rubber of the polymethylene type that utilizes vinylidene fluoride as a comonomer and has substituent fluoro, allyl, perfluoroalkyl or perfluoroalkoxy groups on the polymer chain, with or without a cure site monomer…
> Type 4 – Terpolymer of tetrafluoroethylene, propylene and vinylidene fluoride.
> Type 5 – Pentapolymer of tetrafluoroethylene, hexafluoropropylene, vinylidene fluoride, ethylene, and a fluorinated vinyl ether."[3]

FKM Type 4 – TFE, P, VDF

This polymer is frequently marketed as a base resistant elastomer ("BRE"). Some would argue this claim is misleading since the polymer contains VDF in the backbone which by its very nature is subject to dehydrohalogenation in the presence of a base. The presence of a propylene monomer limits the fluorine content to around 60%. TR10 is reported between -8C to -10C. High temperature ratings are reportedly diminished relative to the other FKM types on account of its lower Fluorine content attributable to propylene ("P") in the backbone.
1) tetrafluoroethylene ("TFE"): $-CF_2CF_2-$
2) propylene ("P"): $-CH_2CH(CH_3)-$
3) Vinylidene fluoride ("VDF"): $-CF_2CH_2-$

This product reportedly offers improved resistance to high amine containing oils and lubes, coolants and transmission fluids as compared to Type 1 and Type 2 FKM's.[4] The Type 4 FKM essentially offers improved base resistance (relative to other FKM's) and can operate at lower temperatures than TFE/P type FEPM class elastomers.

The two commercially available FKM Type 4 materials are examined herein. It should be noted that BRE 7231 is an incorporated bisphenol cure material while Aflas 200P is a peroxide cured material using a TAIC coagent.

FKM Type 5 – TFE, HFP, VDF, E, PMVE

Currently, there appears to be only one commercially available elastomer meeting this classification type. The material is reportedly 65% fluorine by weight and exhibits a TR10 of -7C.
1) tetrafluoroethylene ("TFE"): $-CF_2CF_2-$
2) hexafluoropropylene ("HFP"): $-CF(CF_3)CF_2-$
3) Vinylidene fluoride ("VDF"): $-CF_2CH_2-$
4) perfluoromethyl vinyl ether ("PMVE"): $-CF_2CF(OCF_3)-$

Solvay reports this material "affords excellent resistance to aggressive oils, amine containing fluids, bases, and steam."[5]

[2] ASTM Standard D 1418 – 10a, "Standard Practice for Rubber and Rubber Latices-Nomenclature", section 9, *Annu. Book ASTM Stand.* 09.01, (2011).
[3] Id.
[4] 3M, "BRE 7231" Issued: 6/11 7925HB, 98-0504-1764-5
[5] Solvay, *"Tecnoflon® BR 9151 – Solvay"*, www.solvay.com/en/binaries/TDS_Tecnoflon_BR_9151-216547.pdf, (02/25/2014).

FEPM Difference from FKM

FKM polymers are defined as "Fluoro rubber of the polymethylene type that utilizes _vinylidene fluoride_ as a co-monomer…"[6]. The critical point of distinction between FEPM and FKM is that FKM rubbers contain vinylidene fluoride ("VDF" or "VF$_2$") whereas FEPM rubbers do not. The VDF monomer is a fluorinated vinyl (CH_2CF_2) that has been utilized in fluoroelastomers for more than half of a century. It serves a crucial function in the vulcanization of FKM class elastomers. Specifically, it provides the molecular site through which the polymer can be made unsaturated so that molecular cross-links can be introduced using either a BPAF or TAIC coagent. The unsaturation is typically created through use of a base. Generally, any electron pair donor species ("Lewis base") will suffice. The byproduct of this reaction is hydrofluoric acid ("HF"). This reaction is known as dehydrohalogenation[7] and is documented in most any organic chemistry text. This distinction is extremely important when the practitioner is sealing in a high pH environment. In the oilfield, amines are regularly used to control corrosion associated with H_2S and other corrosive species. This becomes problematic for FKM class rubbers seals since amine corrosion inhibitors will react with VDF segments in the polymer backbone. The polymer will ultimately breakdown with potential corrosion to the seal glands attributable to HF generation that might exceed the capacity of any acid acceptor compounded in the rubber. In the unlikely circumstance that sour hydrocarbons are not inhibited (i.e. no amines introduced), FKM polymers still exhibit significant degradation that will be exacerbated as temperature increases[8]. Both FKM and FEPM class materials exhibit high temperature stability and good chemical resistance.

Commercially Available FEPM

ASTM D1418 does not enumerate "Types" of FEPM polymers. Presently, there is no compelling reason to do so. There are two dominant polymers in the market place classified as FEPM: Aflas 100 series (not the 200P grade) and Viton® ETP. There is considerable difference between these products discussed infra.

AGC introduced Aflas® in 1975. The 150 and 100 grades are a copolymer of tetrafluoroethylene and propylene cured using a peroxide and TAIC coagent.
> 1) tetrafluoroethylene ("TFE"): $-CF_2CF_2-$
> 2) propylene ("P"): $-CH_2CH(CH_3)-$

The composition ratio of the copolymer (C_2F_4/C_3H_6) is 55/45. The polymer's fluorine content is ~57% and its specific gravity is 1.55. TR10 is reported as +3C. Several grades are offered to facilitate applications in extrusions (cable jackets), calendaring (tank linings), and mechanical seals. Aflas offers
> "(1) excellent heat resistance with maximum continuous-service temperature of about 230C and above,
> (2) distinguished chemical resistance with no or little deterioration even in contact with strong acids and
> bases at high temperature, and (3) high electrical resistivity of the order of $10^{15}\sim10^{16}\Omega\circ$cm."[9]

DuPont introduced a terpolymer of TFE, P, and a CSM with an incorporated BPAF cure. The material is known as TBR-605CS (aka VTR-8802). It's fluorine content is ~60% and its specific gravity is 1.7. The polymer is primarily distinguished from the other commercially available TFE/P by an incorporated BPAF cure. VTR-8802 "is inherently resistant to attack by basic chemicals. Provides excellent heat resistance. Provides superior resistance to hydrocarbon oils compared to other TFE-propylene polymers. Provides excellent compression set resistance."[10] This particular material was not examined since previous studies have indicated it is vulnerable in hot aqueous solutions.

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[6] ASTM Standard D 1418 – 10a, "Standard Practice for Rubber and Rubber Latices-Nomenclature", section 9, _Annu. Book ASTM Stand._ **09.01**, (2012). _Emphasis added._

[7] "Organic Chemistry", Solomons, T.W.G., p.167 (John Wiley, 1976).

[8] "Oilfield Polymers and Hydrogen Sulfide", Oilfield Engineering with Polymers, Thomson, Dr. B., MERL Ltd., (Rapra Tech. Ltd, 2006).

[9] AFLAS Fluoroelastomers, AGC literature (2004.09).

[10] VTR-8802 A bisphenol-Cure, Base-Resistant Polymer, DuPont Performance Elastomers, VTE-A10197-00B0204..

In 1997, DuPont introduced a base resistant polymer of TFE, ethylene ("E"), PMVE, and a peroxide sensitive bromine-containing curesite monomer ("CSM") under the brand name Viton Extreme™ ETP[11].

    1) tetrafluoroethylene ("TFE"): $-CF_2CF_2-$

    2) ethylene ("E"): $-CH_2CH_2-$

    3) perfluoromethyl vinyl ether ("PMVE"): $-CF_2CF(OCF_3)-$

Its fluorine content is ~67% and specific gravity 1.82. TR10 is reported as -7C. It is cured using a peroxide and TAIC co-agent. This material is an upgrade from DuPont's previous 900S polymer[12] with a notable distinction of "running cleaner" in terms of less mold fouling. DuPont also reports a higher modulus at extensions beyond 50%[13].

Viton® ETP is most remarkable for its resistance to bases (e.g. amine inhibitors), acids (e.g. HCl), low molecular weight carbonyls (e.g. MIBK, MEK, MTBE, etc), Alcohols (e.g. methanol), aromatic hydrocarbons (e.g. diesel, toluene, etc) as well as many other organic species.

ETP has a remarkably broad chemical resistance. It possesses the resistance exhibited by TFE/P compositions but also resists aromatic hydrocarbons, esters, aldehydes, and ketones (albeit with modest swelling). ETP also offers lower temperature capability than TFE/P. However, this performance comes at a price since ETP costs roughly 10 times an equivalent weight of TFE/P.

EXPERIMENTAL

OBJECTIVES

Two primary objectives were sought: 1) verify the claim of "base resistance" for five fluorelastomers currently positioned as "base resistant", and 2) compare and evaluate the same five "base resistant" fluoroelastomers with regard to stability in commonly encountered oilfield fluids, specifically methanol, aromatic hydrocarbons (eg. Toluene), and seawater.

First, base resistance was tested by aging D412 Die C dumbells in a 40% aqueous solution of dimethylamine. Dimethylamine was selected as a proxy for otherwise proprietary amine compounds utilized in oilfield corrosion inhibitors. Since dimethylamine is a reactive species, tensile data was compiled per D471-16 section16 after aging to determine the extent of interaction.

Second, methanol serves a number of purposes in the oilfield, including hydrate prevention, as a base ingredient for corrosion inhibitors, and use in drilling mud to name a few. Methanol is not reactive with fluorelastomers, but it is soluble in many elastomers. Therefore, volume change was determined per ASTM D471-16 section 12.

Third, toluene was selected as a proxy for aromatic hydrocarbins. Substantial volumes of BTEX solvents (products containing benzene, toluene, ethylbenzene or xylene) are used in oilfield operations such as cleaning out oil-based drilling mud prior to completions, dissolving and dispersing paraffin and asphaltene, and as preflushing in acidizing and cementing procedures. Xylene and toluene are particularly effective solvents with their ability to dissolve paraffins and asphaltenes. Toluene was selected as the less offensive aromatic structure to test the candidate materials. Toluene is not specifically reactive with fluoroelastomers but it is soluble in many of them. Therefore, volume change was determined per ASTM D471-16.

Fourth, aging in seawater was examined. It is frequently joked (and often true) that oilfield operations primarily produce water with a bit of oil included. The six most abundant ions in seawater are chloride (Cl^-), sodium (Na^+), sulfate (SO_4^{2-}), magnesium (Mg^{2+}), calcium (Ca^{2+}), and potassium (K^+). By weight these ions make up about 99 percent of all sea salts.[14] These cations can catalyze and/or participate in any number of reactions. Aging in seawater was analyzed per ASTM D471-16.

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[11] Formerly known as VTR-8710.

[12] "Viton® Extreme™ ETP-600S", DuPont Performance Elastomers, VTE-A10307-00-A0604 (2005).

[13] Id.

[14] https://www.britannica.com/science/seawater

STRAIN ENERGY DENSITY

Strain Energy Density offers a unique means of evaluating the retention of viscoelastic properties under tension by simultaneously accounting for change in tensile strength (integrity) and change in elongation (extensibility). Auda and Hazelton[15] 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.

Eq. (1) Fractional Strain Energy at Break = (TAB x EAB)$_{aged}$ / (TAB x EAB)$_{original}$
where TAB is tensile at break and EAB is elongation at break.

We incorporate an important distinction from the work of Auda and Hazelton. Specifically, we examine fractional strain energy as derived from an integration of the area under each specimen's stress strain curve up to 20% strain, whereas Auda and Hazelton examine the relative area under the stress-strain curve up to the point of the test specimen's breakage. Strain Energy calculated at 20% strain offers two distinct advantages. First, data is derived from the hyper-elastic region of the stress-strain curve offering better insight as to the integrity of the elastomer network as opposed to filler interactions. Second, 20% strain is a more realistic approximation of strain the elastomer will be subject to given generally accepted design guidelines.[16]

Strain energy density was calculated using ASTM D412 Die C dumbells drawn under tension using an Instron.

EXPERIMENTAL METHOD

Table 1 below summarizes the test conditions, and Fig. 1 shows a cutaway view of the test fixture.

Variable	Description
5 "high temperature" base resistant elastomers	(See Table 2 for details)
3 Test Times	22-hours
	70-hours
	168-hours (1-week)
4 Test Fluids	40% Dimethylamine & water by wt.
	Methanol
	Toluene
	Sea water
2 Temperatures	22°C – Toluene, Methanol, Dimethyleamine
	150°C - Seawater
Samples per Set of Test Conditions	D412 Die C Dumbells

Table 1: Experiment parameters

Aging in dimethylamine was conducted to ASTM D471-16 section 8 ("Apparatus") and ASTM D471-16 section 16 ("Change to Tensile Sterengthm Elongation, and Hardness").

The seawater aging vessel, Fig. 1 was designed to offer a bi-metallic environment capable of containing fluids at elevated temperature. The bi-metallic nature of the vessel introduces a small electric potential as one would encounter in a downhole environment. Three (3) D412 Die C dumbells were fully submersed in seawater and aged under temperature in the vessels. Their average was reported. The specimens in a given fixture were manufactured from a single batch of a single rubber compound.

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[15] [15] R.S. Auda, D.R. Hazelton, "Ethylene Propylene Elastomer technology for Improved High Temperature Serviceability", Elastomers Technology Div., Exxon Chemical Co., Paper No. 750962.

[16] Hertz III, D. L. "Thermal Limitations of BPAF cured and TAIC cured Fluoroelastomers Evaluated using Strain Energy Density ", Rubber Division, American Chemical Society, Paper No. 28 (May 2005).

The assembled test cylinder, per Figure 1, was placed in an oven and aged for a specified amount of time at 150°C.
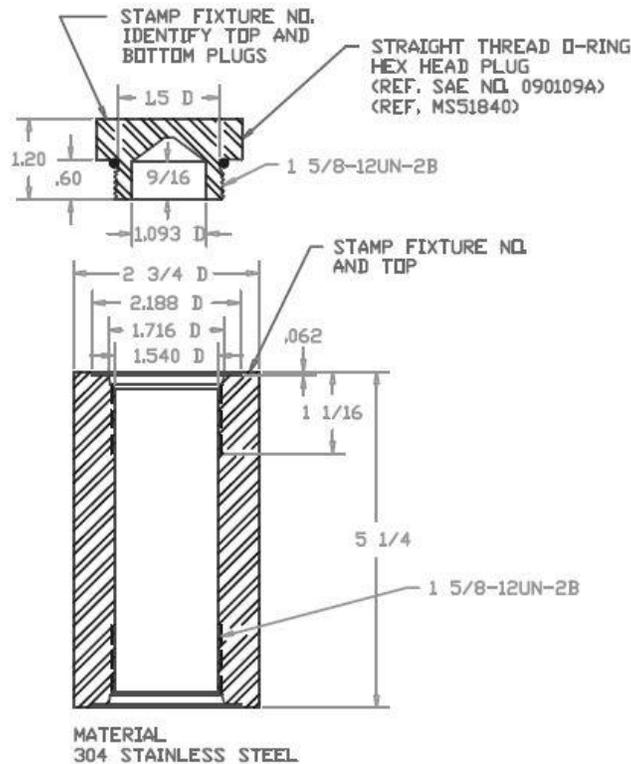

Figure 1: Seawater aging vessel

The base polymers of compounds tested are hereafter referenced as illustrated in Table 2.

Trade Name	Polymer	% Fluorine By weight	Tg[17]	D1418 Designation	Referenced As
AFLAS®	TFE / P	57%	+5°C	FEPM	Aflas
Aflas 200P	TFE / P / VDF	60%	-6°C	FKM Type 4	200P
BRE 7231	TFE / P / VDF	60%	-9°C	FKM Type 4	7231
Viton® Extreme	TFE / E / PMVE	67%	-7°C	FEPM	ETP
BR 9151	TFE / HFP / VDF/ PMVE	65%	-5°C	FKM Type 5	9151

Table 2: Material Designations

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[17] Measured using DSC to ASTM D7426-08 (-40°C to 100°C @ 10°C/min)

Test compounds were designed with the following objectives: 1) reflect the manufacturers' recommendations; 2) mimize variation in composition other than the base polymer; 3) utilize 30 parts N990 as a test standard for a more uniform modulus across the polymer types.

Manufacturer's recommended post cures were utilized.

Aflas 100H			Viton ETP					
Constituent	**PHR**		**Constituent**	**PHR**				
Aflas 100H	100		ETP 600S	100				
MT Black (N990)	30		MT Black (N990)	30				
TAIC	5		TAIC	3				
Vulcup R	1		ZnO	3				
Sodium Stearate	1		Luperox 101XL45	3				
Post Cure: 4 hrs @ 200°C			Post Cure: 16 hrs @ 200°C					

Table 3: FEPM Test formulations

BRE 7231 (Type 4)			Aflas 200P (Type 4)			BR 9151 (Type 5)	
Constituent	**PHR**		**Constituent**	**PHR**		**Constituent**	**PHR**
BRE 7231	100		Aflas 200P	100		BR 9151	100
MT Black (N990)	30		MT Black (N990)	30		MT Black (N990)	30
Maglite D (MgO)	9		TAIC	5		TAIC	4
Struktol WS-280	2		Vulcup R	1		ZnO	5
			Maglite D (MgO)	3		Luperox 101XL45	3
			Sodium Stearate	1			
Post Cure: 16 hrs @ 230°C			Post Cure: 24 hrs @ 230°C			Post Cure: 16 hrs @ 200°C	

Table 4: FKM Test Formulations

Results

DIMETHYLAMINE

Aging in dimethylamine was performed in a very concentrated solution that would not normally be encountered in the oilfield. A secondary amine (two substituted alkyl groups: Me_2NH) was utilized as a proxy for customarily proprietary amine constructs in corrosion inhibitors. The test solution deliberately presented a significantly greater concentration in order to expedite any reactions that would be encountered by these elastomers in the presence of other amines. This aggressive test solution purposefully degraded properties at a significantly more rapid rate than would otherwise be experienced in the field. The objective was to sort the relative performance of these materials when subject to amines.

Mechanical attributes are reported as "Percent (%) Retained" rather than absolute values to better illustrate each material's stability in the specified media. The *percent retained* value is calculated per Equation 2.

Eq. (2) Percent Retained Attribute value = (Attribute value)$_{aged}$ / (Attribute value)$_{unaged}$

PERCENT RETAINED STRAIN ENERGY DENSITY:

Aflas 100H, exhibited the most stable strain energy density in the presense of a strong base. While ETP exhibited an initial decline, the material showed subsequent stability in the strong base. A significant divergence in stability between 200P and 7231, both Type 4 FKM's, was observed. There is a possibility that the BPAF cure utilized in 7231 is susceptible to a strong base. Furthermore, TAIC is a trifunctional coagent whereas BPAF is difunctional, thus TAIC offers 50% more cross-link potential than BPAF within the polymer network that is otherwise exhibiting chain scission. Nevertheless, base resistance is primarily a function of the polymer rather than the cure since BR9151 uses a TAIC coagent yet its mechanical strength was significantly diminished.
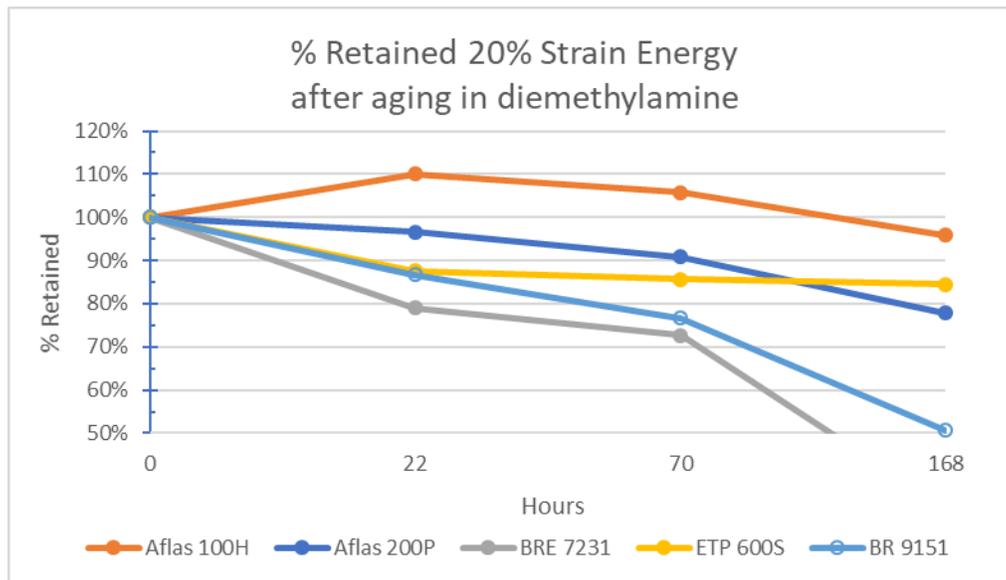

Figure 2: Percent Retained Strain Energy Density after aging

PERCENT RETAINED M25

Modulus at 25% strain, also referred to as M25, was determined per ASTM D471 from ASTM D412 Die C dumbells and reported as percent retained value. M25 is of considerable interest since a 25% strain is frequently encountered in sealing applications, albeit more often under compression than tension. An appreciable reduction in M25 suggests chain scission. Changes in M25 closely mimicked reported strain energy density values. This is to be expected since SED is in part determined by modulus at 20% strain.
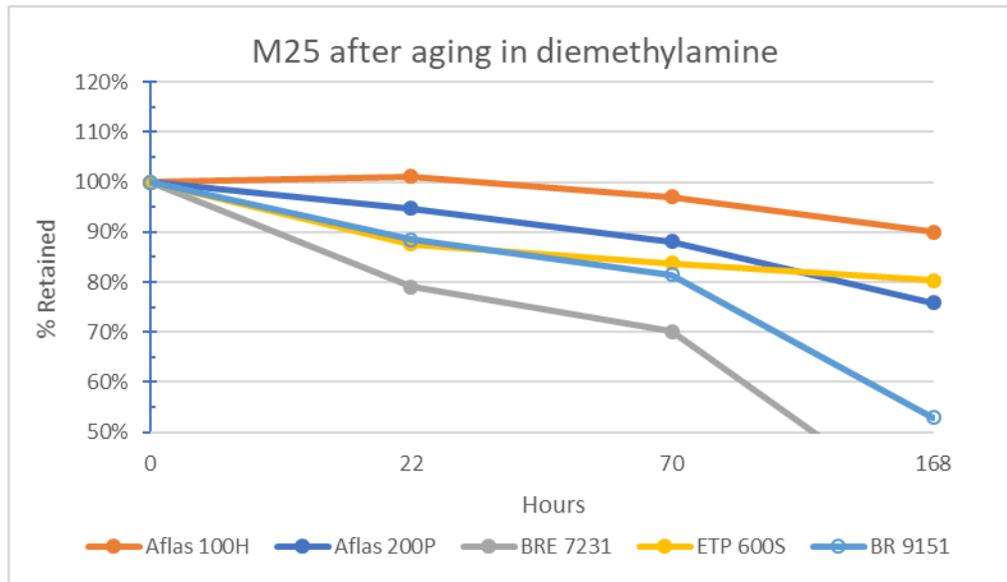
Figure 3: Percent Retained M25 after aging

PERCENT RETAINED TENSILE AT BREAK

Tensile at Break (TAB) was determined per ASTM D471 from dumbells and reported as percent retained value. While the TAB attribute does not have a meaningful relationship to any sealing design it is nevertheless frequently utilized in material specifications and therefore it is reported herein. It is worth noting that ASTM D2000-12[18] allows up to a 30% change in tensile at break for the purpose of classifying materials.

The two FEPM class materials exhibited the highest retention of tensile at break. With the exception of 200P, the FKM class materials, despite their claim of base resistance, exhibited a meaningful loss in strength. Aflas 200P exhibited a remarkably higher retention of TAB relative to the other so-called base resistant FKM's.

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[18] ASTM Standard D 2000 – 12, "Standard Classification System for Rubber Products in Automotive Applications", section 9, *Annu. Book ASTM Stand.* 09.02, (2012).
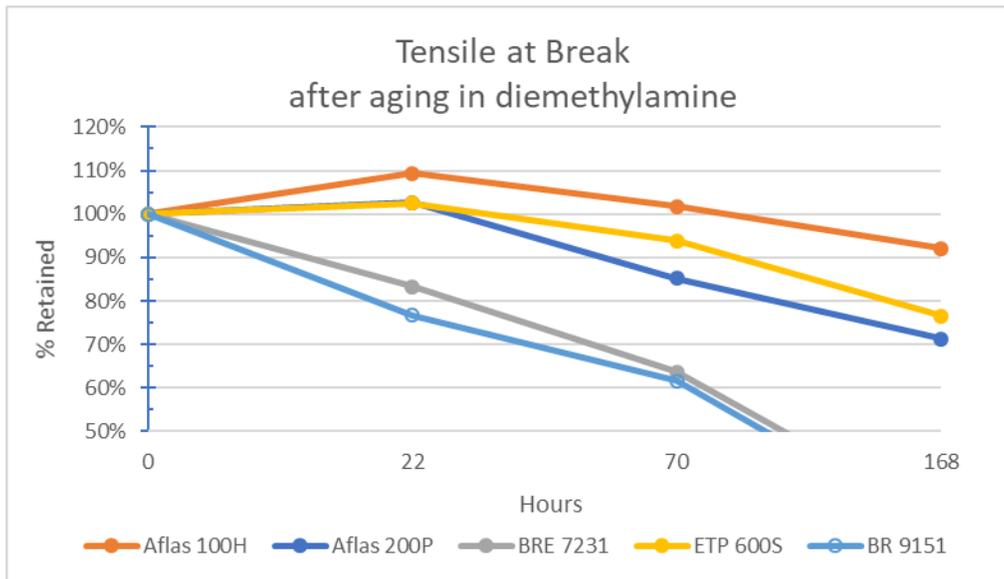
Figure 4: Percent Retained Tensile at Break after aging

PERCENT RETAINED ELONGATION AT BREAK

Elongation at Break (EAB) was determined per ASTM D471 from dumbells and reported as percent retained. The EAB attribute usually does not have a meaningful relationship to a sealing design but remains a valid and easily calculated indication of extensibility. It is worth noting that ASTM D2000-12 allows upto a 50% reduction in elongation at break for the purpose of classifying materials[19]. Significant changes to EAB are indicative of adverse aging characteristics. The 9151 exhibited the greatest change in extensibility.
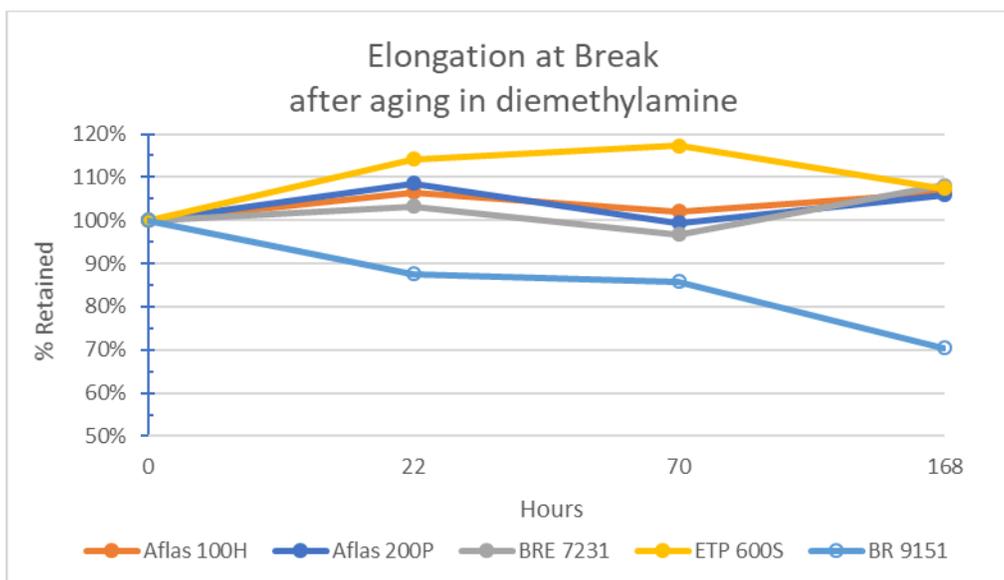
Figure 5 - Percent Retained Elongation at Break after aging

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[19] Id. The author recognizes that D2000 is for automobile applications and does not endorse or agree with the application of D2000 to oilfield applications. Nevertheless, where guidelines/rules are absent, reference to existing standards offers some guidance.

COMPATIBILITY WITH METHANOL AND TOLUENE.

Volume change in both solvents was conducted at room temperature (22C), fully immersed. Volume change was calculated per ASTM D471-16 sections 12 and 18.
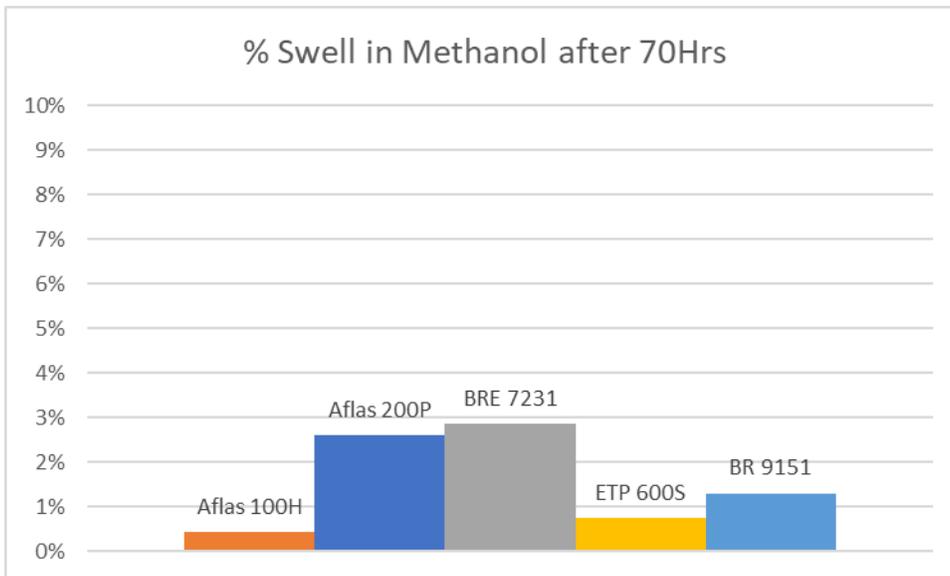

Figure 6 - Percent Volume Change in methanol

None of the materials swelled significantly in methanol. All five materials exhibited swell less than 3% after soaking for 70 hours.
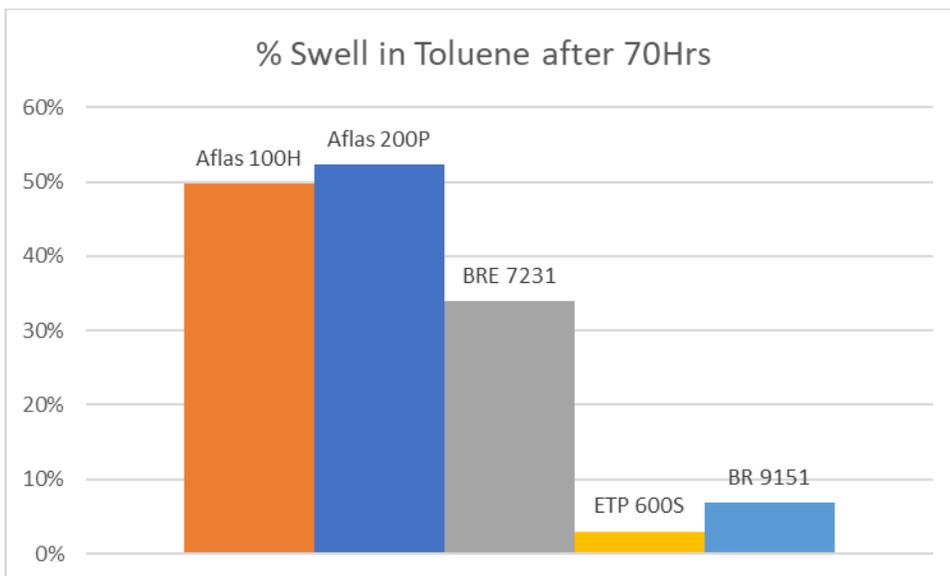

Figure 7 – Percent Volume Change in toluene

It is noteworthy that swelling in toluene is roughly inversely proportional to fluorine content by weight (see table 2): the more fluorine by weight, the less less swelling observed.

SEAWATER

Seawater aging of all samples took place at 150°C, fully immersed. The mechanical attributes of SED, M25, TAB, and EAB were examined after aging.

Mechanical attributes are reported as "Percent (%) Retained" rather than absolute values to better illustrate each material's stability in the specified media. The *percent retained* value is calculated per Equation 2.

PERCENT RETAINED STRAIN ENERGY DENSITY:

The polymers whose backbones include alternating TFE and propylene exhibited the greatest stability in seawater from the perspective of SED and M25. The other candidates exhibited good retention within +/- 20%.
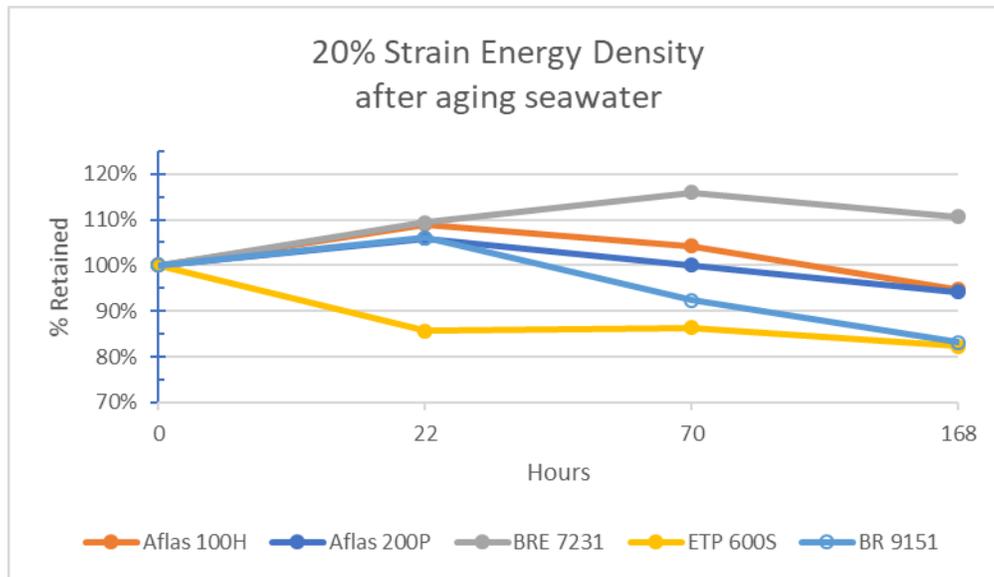

Figure 8: % Retained Strain Energy Density after aging
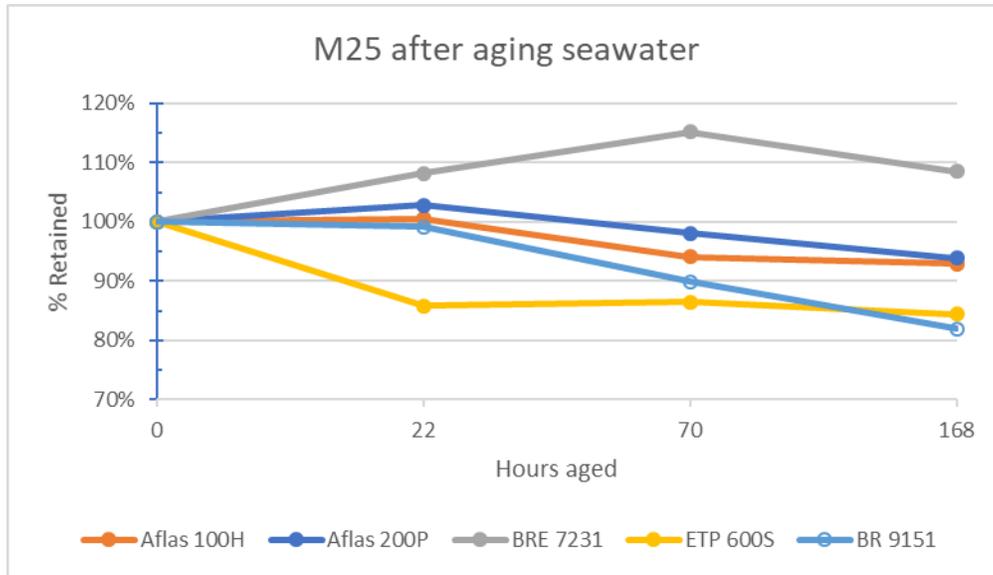
PERCENT RETAINED M25

Figure 9: % Retained M25 after aging

PERCENT CHANGE IN TENSILE AT BREAK

The FEPM polymers exhibited the greatest retention of tensile at break after aging in seawater. The BPAF cured candidate exhibited the least retention.
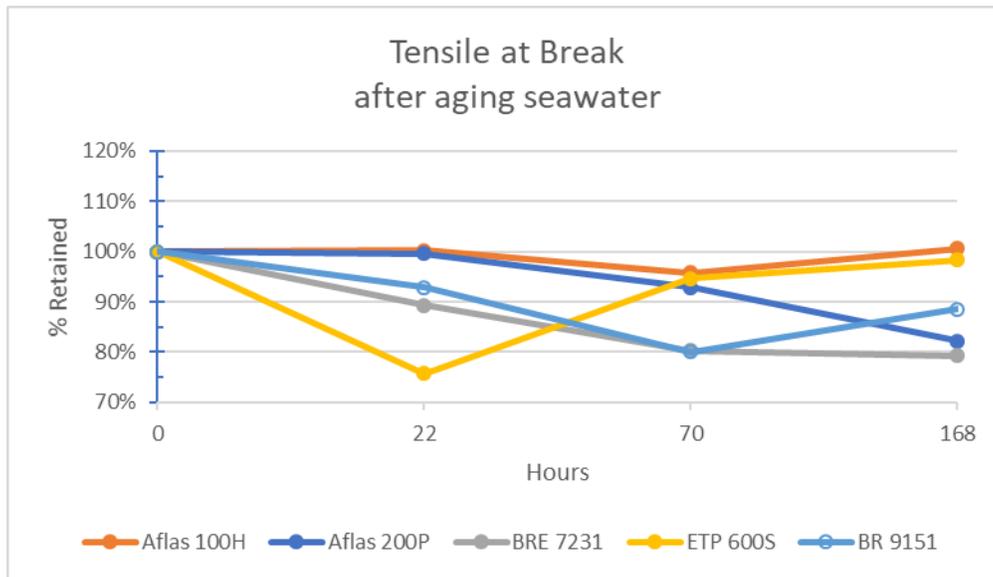

Figure 10: % Retained Tensile at Break after aging
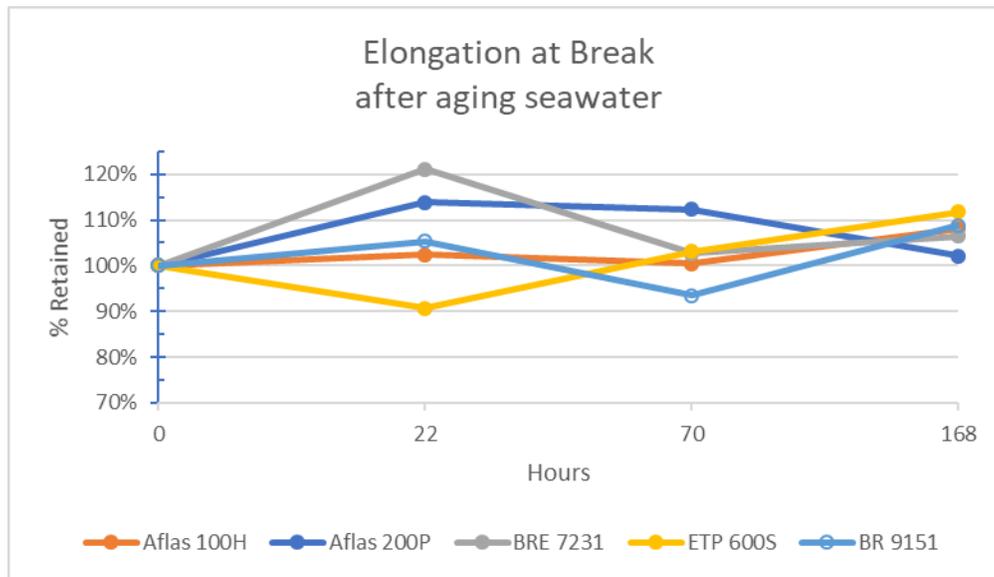
PERCENT CHANGE IN ELONGATION

Figure 11: % Retained Elongation at Break after aging

ELASTOMER SUMMARY

Summary results are tabulabted below in absolute value of percentage change for each attribute after aging 168 hours. Absolute values are presented in this summary since relative stability is the desired trait. Color coding is used to assist the reader.

		Aflas	200P	7231	ETP	9151
Dimethylamine						
SED		4.2%	22.2%	67.3%	15.6%	49.3%
M25		10.0%	24.2%	67.1%	19.7%	47.1%
TAB		7.9%	28.8%	70.1%	23.5%	73.2%
EAB		6.6%	5.9%	8.1%	7.4%	29.6%
Seawater						
SED		5.3%	5.9%	10.7%	17.8%	16.9%
M25		7.1%	6.2%	8.5%	15.6%	18.1%
TAB		0.6%	17.9%	20.7%	1.7%	11.4%
EAB		8.2%	2.1%	6.5%	11.7%	8.9%
Methanol		0.7%	3.4%	3.6%	1.4%	1.8%
Toluene		46.9%	50.8%	33.2%	4.5%	8.4%

SCALE	
<=10%	Good
11 - 20%	OK
21 - 30%	Caution
>30%	Avoid

Table 5: Comparative Results of percentage change in value

CONCLUSIONS

There is no universally accepted definition of "base resistance". However, Aflas 100H exhibited remarkable retention of properties in the presence of dimethylamine, a strong base. Aflas 200P, counter to the prevailing body of data on VDF containing elastomers vulnerability to amines, proved more resistant than other FKM polymers claiming "base resistance". In environments where a strong base(s) will be encountered, Aflas (100 series) and Viton ETP warrant first consideration. Type 5 FKM is clearly not base resistant and caution should be exercised considering a Type 4 FKM, with 200P exhibiting the best stability of the FKM's evaluated.

All five materials performed well in 150C seawater. However, care should be taken considering an elastomer utilizing a BPAF cure system, such 7231 included in this study. Time and again, BPAF cures are susceptible in hot aqueous environemnts.

In a high pH, hot aqueous environment, with a high aromatic hydrocarbon concentration, consideration should be given to utilizing Viton® ETP.

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TRADEMARKS

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