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A Fluoroelastomer Compendium for the Non-metallic Practitioner.

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Forward

This paper's objective is to provide the aspiring rubber technologist a collection of information that will help rationalize the marketplace of popular fluorelastomers and offer guidance on selecting the proper fluoro-elastomer for a sealing application. This paper is directed towards the application engineer rather than the compounder, although both may find the information useful. Polymer supplier references, including their trademarks and brands, are included to help provide more transparency regarding the polymer composition along with its prescribed and proscribed uses. As such, trademarks will be mentioned (and properly acknowledged). This is neither a recommendation nor condemnation of any brand: they are only offered as examples. The brands and grades are not entirely comprehensive. The reader is urged to always consult the polymer manufacturers' specifications and reccomendations.

Cold temperature operability is a topic that can involve considerable debate. Hertz III, in his paper titled "Effects of Low Temperature on the Contact Stress of High Temperature Service Elastomers"[1], illustrates how much variation there can be in the measurement of the glass transition point ("Tg") and whether it accurately predicts operability at cold temperatures. So, for purposes of this paper the attribute of TR10[2] will be used since it is uniformly measured to a standard and widely reported by the polymer suppliers. Nevertheless a caveat remains: there are numerous discrepancies in supplier documentation of TR10 for many of the elastomer grades.

Introduction

ASTM has established nomenclature for the designation of rubber. Several classes are defined by ASTM D1418-10a. Although certain rubber of the "M", "Q", and "Z" classes of elastomers contain fluorine or fluorine substituent groups on the polymer chain, this paper focuses on the "M" class. More specifically, the FKM, FEPM, and FFKM classifications of elastomers are examined. 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…"[3].
>
> "FFKM – Perfluorinated rubbers of the polymethylene type having all fluoro, perfluoroalkyl, or perfluoralkoxy substituent groups on the polymer chain; a small fraction of these groups may contain functionality to facilitate vulcanization."[4]

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[1] D.L. Hertz III, "Effects of Low Temperature on the Contact Stress of High Temperature Service Elastomers", Oilfield Engineering with Polymers, Cavendish Conference Centre, London, England (Oct 2008).

[2] ASTM Standard D 1329 – 08, "Standard Test Method for Evaluating Rubber Property-Retraction at Lower Temperature (TR Test), section 9, *Annu. Book ASTM Stand.* 09.01, (2011).

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

[4] Id.

> “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 1 – Dipolymer of hexafluoropropylene and vinylidene fluoride.
>
> Type 2 - Terpolymer of tetrafluoroethylene, vinylidene fluoride, and hexafluoropropylene.
>
> Type 3 – Terpolymer of tetrafluoroethylene, a fluorinated vinyl ether, and vinylidene fluoride.
>
> Type 4 – Terpolymer of tetrafluoroethylene, propylene and vinylidene fluoride.
>
> Type 5 – Pentapolymer of tetrafluoroethylene, hexafluoropropylene, vinylidene fluoride, ethylene, and a fluorinated vinyl ether.”[5]

Performance (mechanical attributes) Comparison

The general performance of any rubber compound will be dictated by the polymer. There are no “magic tricks” to make an incompatible polymer work in an application. Nevertheless, discussing performance characteristics is problematic because of the myriad compounding and fabrication techniques that can affect various mechanical attributes (e.g. modulus, compression set, stress relaxation, etc) of the material. For instance, there are good TFE/P compounds and there are bad ones. However, all TFE/P compounds will be base resistant[6]. Thus, this paper will avoid discussing tensile strength, modulus, and similar mechanical assessments. Focus will remain on chemical stability and thermal limits.

Cure systems for fluoroelastomers

A discussion of fluoroelastomers must include a consideration of the cure system. When an elastomer fails, it is either through polymer backbone, the cure-site (co-agent), or both. Therefore, understanding the strengths and weaknesses of the cure is as important as selecting the correct polymer.

There are three primary types of curatives for fluoroelastomers: 1) bisphenol, 2) diamine, and 3) peroxide in conjunction with either a co-agent or the presence of a cure-site monomer in the polymer backbone. All three cure systems ultimately require an unsaturated bond(s) through which chemical linkage is achieved. Unsaturation (i.e. a carbon double bond) is achieved by either polymer heat treatment, dehydrohalogenation of a vinylidene fluoride (“VDF”) monomer if it is present, or halogen displacement (usually a bromine or iodine) if a cure site monomer has been polymerized in the elastomer.

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[5] Id.

[6] There have been stories of compounders blending FEPM with FKM to reduce cost. Subsequently, in a high pH environments there have been adverse consequences.

Each type of cure has its strengths and weaknesses. Consideration should be given to the type of operating environment since no cure system is universally good. The predominant operating environment, or the material properties sought, should guide the practitioner in selecting an appropriate elastomer and cure system combination.

Diamine Cure

Diamine cures were introduced in the 1950's and are based upon an organic species containing two amine groups. The earliest diamine cure was known as hexamethylene diamine carbamate. The molecule is a hexamethylene hydrocarbon chain terminated with amine functional groups (one being a carbamate). This cure is best known for its excellent ability to enhance FKM bonding to metal[7] and imparting high hot tensile strength[8].

Bisphenol Cure

The bisphenol cure system, specifically Hexafluoroisopropylidene-bis (4-hydroxy benzene) or BPAF, was introduced by DuPont in the 1970's. It is frequently incorporated into the polymer. The bond is ionic in nature and involves an ether linkage. The bond is difunctional (i.e. two bonds per molecule) in structure. Stevens & Ferrandez indicate that compression set characteristics are excellent compared to the other two FKM curatives.

Hertz III, in his paper "Thermal Limitations of BPAF cured and TAIC cured Fluoroelastomers Evaluated using Strain Energy Density"[9] highlighted the difference in effects of three types of operating environments and observed the following:

> The greatest thermal stability in mineral oil [i.e. aliphatic hydrocarbon] at elevated temperatures was exhibited by the FKM-BPAF composition. The TAIC cure is characteristically unstable in mineral oil at temperatures of 250C and above.
>
> The composition offering the greatest thermal stability up to 336 hours in dry heat at temperatures up to 275C is the FKM-BPAF composition. The BPAF cure is characteristically more stable than the TAIC cure at dry heat temperatures of 225C and higher.

Peroxide Cure

The "peroxide cure" is a misleading label since it typically involves a co-agent, usually triallylisocyanurate (TAIC), with a peroxide serving to initiate the reaction. The bond is covalent in nature and trifunctional (i.e. three bonds per molecule) in structure. Stevens & Ferrandez indicate that a peroxide cure offers excellent resistance to water, steam, and acids.

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[7] R.D. Stevens & P.A. Ferrandez, "Fluorocarbon Elastomer", p.374, The Vanderbilt Rubber Handbook (14th Ed. 2010)

[8] DuPont™ Viton® Selection Guide, Technical Information (Rev. 7, July 2010). Reference No. VTE-H68134-00-G0710.

[9] D.L. Hertz III, "Thermal Limitations of BPAF cured and TAIC cured Fluoroelastomers Evaluated using Strain Energy Density", Paper No.28, 167th Technical Meeting of the Rubber Division, American Chemical Society San Antonio, TX (May 2005), ISSN: 1547-1977

Hertz III observed the following characteristic in his paper on "Thermal Limitations"[10] in different operating environments and observed:

> The greatest stability at excessive temperatures in deionized water was exhibited by the FEPM-TAIC composition, which consistently operated in excess of 168 hours at temperatures of 225C to 275C. The BPAF cure system is characteristically unstable in deionized water at temperatures of 225C and above.

Boye & Hertz III, in their paper on "Thermal Stability of Fluorelastomer Crosslinks: Peroxide/Triazine and Bisphenol AF/Onium Cure"[11] observed:

> The TAIC crosslink exhibits a higher percent retained contact stress in all three aging media [water, dry heat, mineral oil] which initially suggests it is more stable in a thermal environment. However, the retained contact stress of the TAIC formula approached that of the BPAF formula after 1500 hours in mineral oil. Furthermore, whereas the measured contact stress of the BPAF formula exhibits no distinct trend over the 1500 hour period, the TAIC formula exhibits a distinct decay in contact stress over the same period in all three aging media.

Commercially Available FKM's

In 1957, DuPont company introduced a dipolymer of hexafluoropropylene and vinylidene fluoride under its tradename of Viton®. It was one of the earliest commercial fluoroelastomer introductions and perhaps the most successful. In the 1960's 3M followed with its Fluorel® brand[12], now known as its Dyneon™ brand. Several other brands followed over the years including DAI-EL™ from Daiken, Technoflon® from Solvay, and AFLAS® from Asahi Glass Chemicals simply to name the more commonly known brands.

Within each brand, suppliers provide grades, usually with specific performance characteristics. Frequently a little "digging" is required to determine the molecular construct. Unfortunately, suppliers seldom categorize their grades to the ASTM D1418 - FKM Types. Furthermore, the proliferation of grades across the several manufacturers of FKM type polymers have produced a vast array of FKM options. Nevertheless, the performance characteristic of any fluoroelastomer grade will always be determined by its molecular constitution, including the type of cross-linking used to produce the final product. Herein lies the helpfulness of ASTM's D1418 framework.

Suppliers generally advertise several attributes to differentiate their grades such as TR10, Mooney viscosity, Curative, specific gravity, and sometimes percent fluorine. Be wary of the customer who bases their selection criteria on percent fluorine alone. Chances are high they do not fully understand what

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[10] Id.

[11] W.F. Boye & D.L. Hertz III, "Thermal Stability of Fluorelastomer Crosslinks: Peroxide/Triazine and Bisphenol AF/Onium Cure", 4th MERL International Conference, Oilfield Engineering with Polymers
London, UK (Nov 2003).

[12] R.D. Stevens and P.A. Ferrandez, "Fluorocarbon Elastomer", The Vanderbilt Rubber Handbook (14th Ed. 2010).

they need and are likely headed for trouble in their application. Fluorine content does not necessarily indicate the best choice of FKM type whose constitution may ultimately determine behavior rather than the percent fluorine by weight. In the discussion on FKM Types, understand that all the types possess excellent heat and oil resistance relative to other classes of polymers.

FKM Type 1 – HFP, VDF

FKM dipolymers, in which vinylidene fluoride (“VDF”) and hexafluoropropylene (“HFP”) monomers are copolymerized, are generally 66% fluorine by weight.

1) Vinylidene fluoride (“VDF”): $-CF_2CH_2-$
2) hexafluoropropylene (“HFP”): $-CF(CF_3)CF_2-$

This type of FKM exhibits a TR10 near -20C. FKM dipolymers are usually referred to as general purpose with the best overall balance of properties. Some suppliers have grades with an incorporated cure while others require the compounder to include the cure system in the formulation. Table 1 lists major suppliers along with the brand and grade under which they sell this type of FKM. Grades are normally preceded with a prefix to help identify the material composition. The ‘#’ is used to indicate additional numbers or letters that serve to identify a specific grade.

Supplier	Brand	Grade prefix	Cure
DuPont	Viton®	A-###	Bisphenol
3M	Dyneon™	FC #### FE ####[13] FG ####	Bisphenol
	Dyneon™	FPO	Peroxide
Daikin	DAI-EL™	G-7##	Bisphenol
	DAI-EL™	G-8##	Peroxide
Solvay	Technoflon®	N ### FOR ###	Bisphenol Bisphenol(incorporated)

Table 1 – FKM Type 1 – Suppliers and their grades

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[13] Dyneon FE 5840Q & FE 5730 is an exception to this observation since it is documented as a terpolymer. 3M Dyneon Fluoroelastomers, Product Guide, Issued 5/17 12321HB, 98-0504-1068-1 Rev. B

FKM Type 2 – TFE, VDF, HFP

FKM terpolymers, so called since there are three monomers copolymerized, are generally 67 – 69% fluorine by weight. This type of FKM exhibits a TR10 around -5C. By altering the ratios of the monomeric units, the percentage of fluorine by weight is altered. To understand this, you need only examine the molecular construct of the three monomeric units and observe the number of fluorine atoms in each unit:

1) Vinylidene fluoride (“VDF”): $-CF_2CH_2-$
2) tetrafluoroethylene (“TFE”): $–CF_2CF_2-$
3) hexafluoropropylene (“HFP”): $-CF(CF_3)CF_2-$

As a general rule, fluid resistance increases as the fluorine content increases. However, as fluorine content increases, cold temperature flexibility decreases. This simple relationship alone explains the preoccupation with fluorine content. Considering the higher fluorine content of a Type 2, there is no surprise that FKM Type 2 offers better resistance in aromatic hydrocarbons (e.g. diesel based muds, asphaltenes), alcohols (e.g. methanol), and engine lubes. Another reported benefit of a Type 2 FKM is better heat resistance[14].

Supplier	Brand	Product Grade	Cure
DuPont	Viton	B-### GF-### F-###	Bisphenol
3M	Dyneon	FT #### FX ####	Bisphenol
Daikin	DAI-EL	G-55# G-6##	Bisphenol
		G-9##	Peroxide
		G-501	Diamine
Solvay	Technoflon	P ### T ### FOR ####	Peroxide Bisphenol Bisphenol(incorporated)

Table 2 - FKM Type 2 – Suppliers and their grades

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[14] D.L. Hertz, Jr., “11. Temperature Resistant Elastomers – D. Fluoroelastomers”, Basic Elastomer Technology, The Rubber Division American Chemical Society (1st Ed. 2001).

FKM Type 3 – TFE, PMVE, VDF

The foremost advantage of Type 3 FKM is its improved cold temperature operability. The manufacturer will not necessarily advertise that you are purchasing a Type 3, but they will likely disclose fluorine by weight in the range of 60% - 65% but more importantly, TR10 values in the range of -20 to -40C. This is typically accomplished by substituting perfluoromethyl vinyl ether (“PMVE”)[15] for the hexafluoroproylene otherwise found in a terpolymer. PMVE[16], structured as -$CF_2CF(OCF_3)$-, with its bulky -O-CF_3 group decreases symmetry of the polymer chain and thus maintains mobility longer as the polymer network contracts at colder temperatures.

1) tetrafluoroethylene (“TFE”): –CF_2CF_2-
2) perfluoromethyl vinyl ether (“PMVE”): -$CF_2CF(OCF_3)$-
3) Vinylidene fluoride (“VDF”): -CF_2CH_2-

Solvay, under their “VPL” grade, introduced a novel variant to this type of FKM using their MOVE technology rather their PAVE technology. Rather than utilizing PMVE they have utilized Perfluoromethoxyvinyl ethers (i.e. CF3-(O-CF2-O)n-CF=CF2).[17] This particular grade possesses a fluorine content up to 67% increasing its resistance to fuel absorption. Furthermore, Solvay claims TR10 as low as -40C can be achieved. Notably, this particular polymer grade breaks the old paradigm of increasing fluorine content reducing cold temperature flexibility by adding multiple ether linkages.

Supplier	Brand	Product Grade	Cure
DuPont	Viton	GLT GFLT	Peroxide
3M	Dyneon	LTFE 6###	Peroxide
Daikin	DAI-EL	LT-2##	Peroxide
Solvay	Technoflon	PL ### VPL ###	Peroxide Peroxide

Table 3 - FKM Type 3 – Suppliers and their grades

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. Fluorine content is around 60%. TR10 is reported between -8C to -10C. High temperature ratings are somewhat diminished relative to the other FKM types on account of its lower Fluorine content attributable to propylene (“P”) in the backbone.

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[15] Solvay utilizes PAVE rather than PMVE in their PL grade. http://www.solvay.com/en/markets-and-products/featured-products/Tecnoflon-FAQ.html (Aug 2017)

[16] https://www.chemours.com/FluoroIntermediates/en_US/products/vinyl_ether_pmve.html (Aug 2017)

[17] http://www.solvay.com/en/markets-and-products/featured-products/Tecnoflon-FAQ.html (Aug 2017)

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.[18] This type of FKM essentially offers improved base resistance (relative to other FKM’s) and can operate at lower temperatures than TFE/P type FEPM class elastomers.

Supplier	Brand	Product Grade	Cure
3M	Dyneon	BRE 7231[19]	Bisphenol (incorporated)
Asahi Glass	Aflas	200P (SPL-FKM)	Peroxide-TAIC

Table 4 - FKM Type 4 – Suppliers and their grades

FKM Type 5 – TFE, HFP, VDF, E, PMVE

Solvay appears to be the only supplier who discloses this composition in their offering. 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.”[20]

Supplier	Brand	Product Grade	Cure
Solvay	Technoflon	BR 9151[21]	peroxide

Table 5 - FKM Type 5 – Suppliers and their grades

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[18] 3M, “BRE 7231” Issued: 6/11 7925HB, 98-0504-1764-5

[19] Id.

[20] Solvay, “Tecnoflon® BR 9151 – Solvay”, www.solvay.com/en/binaries/TDS_Tecnoflon_BR_9151-216547.pdf, (02/25/2014).

[21] R. Villa, “Technoflon FKM and FFKM portfolio: an overview on standard grades and specialties”, Solvay Solexis, Utrecht, (Dec 2009).

FEPM Difference from FKM

FKM polymers are defined as "Fluoro rubber of the polymethylene type that utilizes *vinylidene fluoride* as a co-monomer…"[22]. 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 (a "Lewis base") will suffice. The byproduct of this reaction is hydrofluoric acid ("HF"). This reaction is known as dehydrohalogenation[23] 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 the amine corrosion inhibitors will be absorbed on account of a fundamental thermodynamic principle[24] and will subsequently initiate reactions within the polymer. The polymer will harden and 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 (no amines), FKM polymers still exhibit a loss of mass and hardening that will be exacerbated as temperature increases[25].

Dr. Phil Abrams, of ExxonMobil, studied multiple polymers for an acid gas (65% H2S) reinjection project and observed in Aflas® (FEPM) that an "initial rise in elongation and reduction in modulus, followed by stability, are characteristic and do not indicate chemical ageing."[26]

Like other fluorelastomers, FEPM class polymers generally exhibit low hot tear strength and weak mechanical properties compared to 'R' class materials such as nitrile. Their merits remain high temperature stability and chemical resistance.

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

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

[24] The second law of thermodynamics specifies that the entropy of a closed system increases with time.

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

[26] Dr. P. Abrams, "Seals Selection for Acid Gas Injection using an accelerated Test Program", Oilfield Engineering with Polymers, (Rapra Tech. Ltd, 2006).

Commercially Available FEPM

Aflas was the first commercially introduced FEPM class material. In fact, there was no FEPM designation within ASTM D1418 at the time. The novel and unique attribute of Aflas was the absence of VDF. The importance of this, specifically its remarkable resistance to high pH environments, was gradually realized by the market place and the material gained significant recognition.

A word of caution is in order here regarding product identifications. Some older FKM class DuPont materials used the acronym “TBR”, for total base resistance. This arguably caused some confusion in the market place since these materials, such as TBR-501C, actually contained VDF. By the mere presence of VDF, these materials are technically not base resistant[27]. In the meantime, TBR-605CS is an FEPM class polymer and is in fact totally base resistant.

Furthermore, by boot-strapping the renowned Viton trademark, DuPont inadvertently fueled the rubber class confusion by using a primarily FKM designated trademark for their FEPM class materials. More recent literature distinguishes the DuPont FEPM grades as “Viton® Extreme™”. When discussing DuPont’s base resistant polymers, it is advisable to specify the polymer grade rather than simply the Viton trademark. Thus, you do not simply want to specify Viton® for your sour completion requiring amine corrosion inhibitors but rather ETP for the same.

AGC committed the same trademark boot-strap but in reverse. They used their widely recognized Aflas® (FEPM) trademark to introduce an FKM class material. Fortunately, for the otherwise confused materials engineer, most of AGC’s FKM introduction has been withdrawn with the exception of Aflas 200P. Thus, be alert to the grade of Aflas and understand that an SP or MZ grade is an FKM class material.

There are other misleading acronyms such as BRE (base resistant elastomer) used by Dyneon™[28] that in fact contain VDF and are thus FKM class rubbers. Their base resistance can be left to debate, but the fact remains these grades contain a monomer that is vulnerable to nucleophiles (i.e. high pH solutions).

Structures

ASTM D1418 does not enumerate “Types” of FEPM polymers. At the present time, there is no compelling reason to do so. For clarity, however, a differentiation is made here. Perhaps the most significant difference in commercially available FEPM polymers is that one resists aromatic hydrocarbons while the other does not. The issue is not a reaction with aromatics, but solubility and subsequent swelling.

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[27] W.W. Schmiegel, “A Review of Recent Progress in the Design and Reactions of Base-Resistant Fluoroelastomers”, International Rubber Conference (2003).

[28] Dyneon™ Base Resistant Elastomer BRE 7231X. Issued 1/01.

1. TFE/P type

AGC introduced Aflas® in 1975. The 150 and 100 grades are a copolymer of tetrafluoroethylene and propylene cured using a peroxide and TAIC coagent. 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}~10^{16}Ω◦cm."[29]

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."[30]

Supplier	Brand	Product Grade	Cure
Asahi Glass	Aflas®	100H 100S	peroxide
Dupont	Viton® Extreme™	TBR-605CS (VTR 8802)	bisphenol

Table 6 – FEPM (TFE/P) – Suppliers and their grades

The manufacturers' websites offer a good amount of information regarding chemical compatibility. Definitive sources can be found at www.Viton.com and www.Aflas.com . However, for the most commonly encountered oilfield chemicals, you should be aware of the following.

TFE/P polymers are resistant to high pH organic species including caustics and amines.

TFE/P compositions are known to swell in aromatic hydrocarbons (e.g. diesel), low-polar chlorine solvents, aromatic solvents (toluene, benzene, xylene, etc), and ketones (MIBK, MEK).

On the other hand, they exhibit little if any swelling in methanol and ethanol.

A less known but valuable attribute of TFE/P is its resistance to absorbing CO2. Carbon dioxide is commonly found in natural gas and petroleum reservoirs. Furthermore, the number of seals needed for

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

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

CO2 sequestration projects will only increase given the current political environment. Hertz Jr., in his paper entitled "Elastomers in the Hot Sour Gas Environment"[31] examined the behavior of TFE/P polymers and found them to present the best value proposition in terms of price and performance for withstanding high pressure CO_2 and CH_4.

2. TFE/E/PMVE type (aka "ETP")

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[32]. 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[33] with a notable distinction of "running cleaner" in terms of less mold fouling. DuPont also reports a higher modulus at extensions beyond 50%[34].

Supplier	Brand	Product Grade	Cure
Dupont	Viton® Extreme™	ETP-600S	peroxide

Table 7 – FEPM (TFE/E/PMVE) – Suppliers and their grades

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, alcohols, ester, 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.

High Temperature attributes

High temperature performance is best evaluated in the application context within a test cell. However, comparative performance can be predicted by evaluating material test specimens. In this regard, Hertz III, in his technical paper "Thermal Limitations of BPAF cured and TAIC cured Fluoroelastomers Evaluated using Strain Energy Density", which included TFE/P polymers in the study, concluded:

> "Given the large number of fluoroelastomer options today, careful consideration should be given to both elastomer selection and the cure system for applications requiring continuous high temperature service, as well as those subject to extreme thermal excursions. Temperature, duration of thermal excursions if any, and the operating medium are critical factors to consider at temperatures in excess of 200C.

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[31] Hertz, Jr., D.L, "Elastomers in the Hot Sour Gas Environment", Elastomerics (Sept 1986).

[32] Formerly known as VTR-8710.

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

[34] Id.

> …The BPAF cure system is characteristically unstable in deionized water at temperatures of 225C and above. The greatest stability at excessive temperatures in deionized water was exhibited by the FEPM-TAIC composition, which consistently operated in excess of 168 hours at temperatures of 225˚C to 275˚C…"[35]

The same study also recognized that an FKM is preferable to FEPM in elevated temperature (225˚C+) dry heat or aliphatic hydrocarbons.

Low Temperature attributes

Hertz III studied the contact stress of various elastomers and reported his findings in the paper entitled "Effects of Low Temperature on the Contact Stress of High Temperature Service Elastomers"[36]. Quantitative measurements of glass transition are illustrated in Table 8. The term "dP/dt Increase Temp", explained fully in the referenced paper, indicates the temperature at which a gas leak occurred.

Base Elastomer	TR-10 (°C)	TMA Transition (°C)	DSC Tg (°C)	DMRT Tg (C)	dP/dt Increase Temp (°C)
TFE/P (AFLAS®)	3	2.2	2.3	3.6	-9
TFE/E/PMVE	-7	-8.7	-10.0	-3.2	-23

Table 8 – FEPM Low temperature transition points

In general terms, a TFE/P composition is not recommended for temperatures below freezing. The ETP, on the other hand, can handle temperatures slightly below freezing. Both ETP and TFE/P indicated the ability to continue sealing a gas as temperature dropped below their glass transition point (Tg). However, the PMVE ether linkage and its bulky perfluoro-methyl group increase low temperature mobility of the ETP polymer as evidenced by its lower Tg.

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[35] Hertz III, D.L. "Thermal Limitations of BPAF cured and TAIC cured Fluoroelastomers Evaluated using Strain Energy Density", High Performance and Specialty Elastomers 2005 International Conference; Geneva, Switzerland, (Apr 2005).

[36] D.L. Hertz III, "Effects of Low Temperature on the Contact Stress of High Temperature Service Elastomers", Oilfield Engineering with Polymers, Cavendish Conference Centre, London, England (Oct 2008).

Commercially Available FFKM

ASTM D1418-10a defines FFKM elastomers, more commonly known as perfluoroelastomers, as "Perfluorinated rubbers of the polymethylene type having all fluoro, perfluoroalkyl, or perfluoroalkoxy substituent groups on the polymer chain; a small fraction of these groups may contain functionality to facilitate vulcanization."[37]

Hertz Jr., in his chapter on "Specialty Synthetic Rubbers"[38], summarized the characteristics of perfluoroelastomers as "[t]he presence of hydrogen makes a fluoroelastomer vulnerable to attack by aqueous and non-aqueous electrolytes such as coolants and highly stabilized lubricants. Totally fluorinated elastomer, 'perfluoroelastomer', offers the user a rubbery fluoropolymer with outstanding long-term resistance to heat, solvents, and chemicals."[39]

FFKM's are basically copolymerized tetrafluoroethylene (TFE), perfluoroalkyl vinyl ether ("PAVE"), with an added cure site monomer. Cure site monomers are typically proprietary but can be a fluorinated ethylene with a single bromine or iodine substitution for abstraction and subsequent cross-linking[40].

DuPont was the first to commercially introduce a fully-fluorinated rubber. Their approach to the market was unique since they did not sell uncured polymer, but rather developed a portfolio of FFKM compositions that they molded to either standard o-ring specifications or customer specified designs. To date, uncured Kalrez® is not commercially available. Daiken appears to be adopting a similar tactic through their TOHO KASEI CO., LTD division.

FFKM's are expensive. While Viton ETP is an order magnitude more expensive than an FKM, the typical FFKM is two orders of magnitude more expensive than FKM. The selection of FFKM should be judicious and made only where the other fluoroelastomer options are untenable.

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

[38] D.L. Hertz, Jr., "Specialty Synthetic Rubbers", The Vanderbilt Rubber Handbook, R.T. Vanderbilt Company, Inc. (14th Ed. 2010).

[39] Id.

[40] R. Villa, supra.

1. *Continuous service temperature <225C*

ASTM D1418 does not enumerate "Types" of FFKM polymers. All the perfluoro-rubbers contain excellent broad chemical resistance and are ultimately differentiated by their thermal limits. The use of TAIC in curing this class of materials limits their operating temperature to 225C or less since TAIC structure begins to revert from triallyl to mono-allyl with a consequent loss in properties. Thus, never assume an FFKM will operate at temperatures exceeding the limit of an FKM or FEPM elastomer. The requirement of TAIC or other co-agent should alert the practitioner to the material's thermal limit. For "molded only" FFKM grades, consult the specification sheet.

Supplier	Brand	Product Grade	Cure
Asahi Glass	Aflas®	PM-1100	peroxide
Daiken	DAI-EL®	GA-15 GA-105	
DuPont	Kalrez®	00##, etc.	Molded only
Solvay	Technoflon®	PFR 94 PFR 06HC	peroxide
3M	Dyneon™	PFE 40Z, 60Z, 80Z, 90Z	peroxide

Table 10 – FFKM grades for continuous service < 230C

2. *Continuous service temperature >225C*

The high-temperature FFKM's usually embody a proprietary incorporated cure that may be initiated by a peroxide or proprietary catalyst.

Supplier	Brand	Product Grade	Cure
Asahi Glass	Aflas	PM-3000	peroxide
Daiken	DAI-EL® Perfluor	GA-500	V-6M
DuPont	Kalrez®	1050LF 3065 4###, etc.	Molded only
Solvay	Technoflon®	PFR 95HT	peroxide
3M		PFE 7502BZ PFE 81TZ PFE 1###TZ PFE 1###TBZ	PFE 01CZ

Table 11 – FFKM grades for continuous service > 230C

3. *Ultra Pure*

Perfluoroelastomer seals can be used in equipment for the manufacture of semiconductor, pharmaceutical, and food stuffs. These industries have demanding requirements restricting the amount of extractable substituents. Consequently, specialty grades are manufactured to meet these requirements.

Supplier	Brand	Product Grade	Cure
TOHO KASEI CO., LTD(Daiken)	Dupra™	DU ###	Molded only
DuPont	Kalrez®	6###, etc.	Molded only
Solvay	Technoflon®	PFR 59XX	peroxide

Table 12 – FFKM grades for continuous service > 230C

Conclusion

Fluoroelastomers have been a valuable development in the sealing business since the 1950's. Fortunately, ASTM has offered a brand independent classification system for rationalizing the fluoro classes of elastomers despite a bewildering array of brands and grades. While FKM type elastomers dominate the landscape for high-temperature, chemical resistant elastomers, the FEPM and FFKM class of elastomers also serve critical and distinct applications. If the practicing engineer understands the limits of the available fluoroelastomers, they can be utilized to solve sealing problems that might otherwise be chronic.

- D.L. Hertz III

The author invites polymer manufactures to submit any corrections, additions, or clarifications to this work for future revisions to info@sealseastern.com

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