TECNOFLON®
A GUIDE TO FLUOROELASTOMERS

TECNOFLON Fluoroelastomers

Solvay Solexis

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A Guide to Fluoroelastomers

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By Steve Jagels

Introduction

This guide is written for rubber manufacturers, seal designers, engineers, and chemists interested in fluoroelastomers (FKM). While this guide offers detailed information and practical advice, there is no substitute for the experience of your FKM supplier's Technical Service Engineer.

Background

Fluoroelastomers are known for their broad chemical and heat resistance. Despite FKM's higher cost compared to other elastomers, they are often the first choice in demanding seal environments and they approach the ideal for a universal sealing material. Fluoroelastomers are indispensable to the automotive , aerospace, the chemical process industries, and other exacting uses.

Markets and Applications

Automotive

The automotive industry has become one of the largest consumers of FKMs. Fluoroelastomers are resistant to oils, lubricants, fuels, oxygenate additives, and high temperatures. Fuel permeation through fluoroelastomers is the lowest among all elastomers, a quality necessary to meet environmental regulations for vapor emissions. Fluoroelastomers are unmatched in performance and seal reliability thereby reducing warranty claims and extending vehicle life. Typical FKM parts include shaft seals, valve stem seals, O-rings, engine head gaskets, intake manifold gaskets, fuel pump diaphragms, water pump gaskets, turbo chargers, fuel hoses, exhaust and pollution control seals.

Aerospace

The reliability of FKMs is unrivaled in fuels, lubricants, and special fluids used in aerospace. Compression set resistance, high temperature resistance, and low outgassing are typical requirements for aerospace applications. FKMs are fire resistant and self-extinguishing which is ideal in high oxygen environments such as vehicle cockpits. Other parts used in the aerospace industry which are made from fluoroelastomers are shaft seals, hydraulic hoses, fuel tanks, electrical connectors, firewall gaskets, and hot engine lubricant traps.

Oil Drilling

Thermal stability, resistance to sour gas, steam, and amine corrosion inhibitors make FKMs ideal for down hole environments. High molecular weight FKMs are resistant to explosive decompression and high pressure extrusion. Fluoroelastomers can be compounded for excellent resistance to hydrogen sulfide and conventional drilling fluids. Typical parts include blowout preventors, packers, and valve seats.

Chemical Process Industry

Severe chemical and thermal environments are prevalent in this industry. Seal reliability is paramount to productivity and environmental safety. Typical parts include hoses, gaskets, diaphragms, tank linings, and O-rings.

Energy

FKMs resist acid flue duct emissions. FKM expansion joints are commonplace throughout this industry where high temperature performance and resistance to corrosive gases and particulates is required.

Coatings and Linings

Coated rollers for photocopiers and the textile industry are common applications. Also, FKMs are used for coatings in stacks and ducts where sulfur dioxide high temperature exhaust gases are present.

Flares

FKMs are used as a binder with reactive metal powders to increase infrared bands in military flares.

Plastics Industry

Fluoroelastomers work exceptionally well as process aids in polyolefin plastics such as PP, HDPE, and LLDPE. Adding copolymers in amounts ranging from 0.05-0.2% reduces melt fracture. This prevents “shark skin” and increases productivity and appearance.

General FKM Properties	
Specific Gravity	1.81 to 1.90
Fluorine Content	66 to 70%
Chemical Resistance	Broad Range of Chemicals, Gasoline, Alcohol Fuel Additives, Acids, Oils, Ozone, Radiation, Non-Burning in Air
Temperature Range	-30° to 275°C
ASTM Designation	HK
Not Recommended for	Ammonia, Low Molecular Weight Esters and Ketones, High pH Environments

Figure 1.

FKM Manufacturing

Fluoroelastomers are manufactured using a series of complex steps and chemical reactions. The raw materials are toxic and explosive, therefore the cost of fluoroelastomers is higher compared to other elastomers. Figure 2 is a simplified diagram of some of the major steps involved in FKM manufacturing.

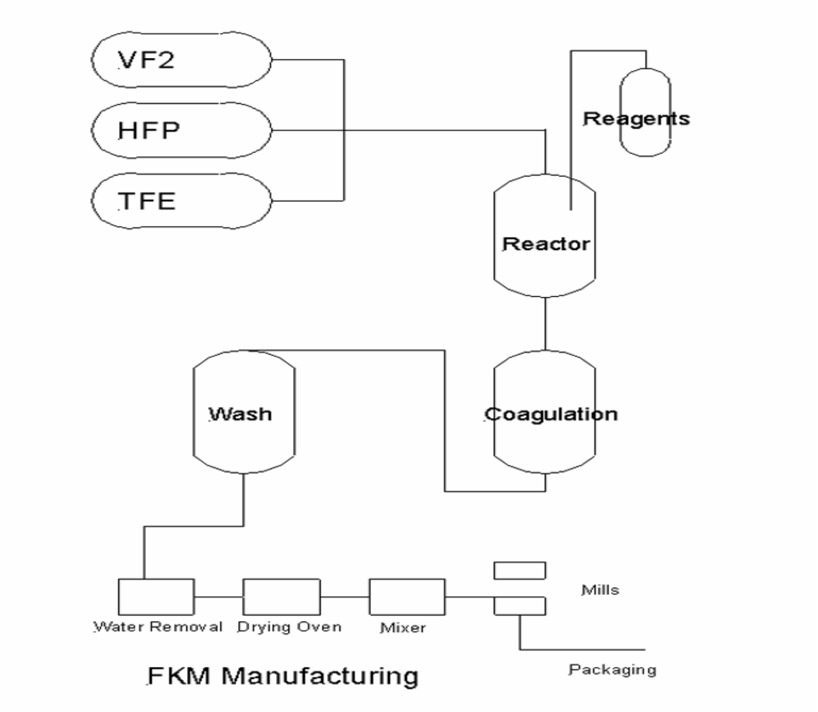


Figure 2.

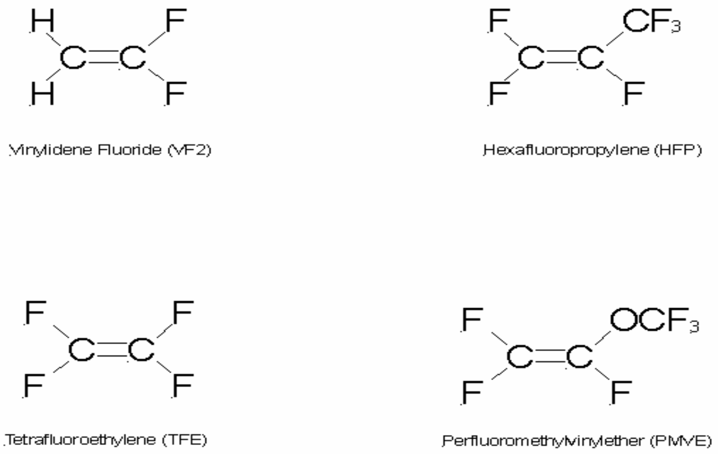
Fluoroelastomer Types

Fluoroelastomers are divided into broad categories based on several factors. Typically the monomer composition, cure mechanism, and curative level divide the classes. From these classes, generalizations usually can be drawn on the mechanical/physical properties, fluid and heat resistance, and processing characteristics.

Recent advances in polymerization technology offer major performance improvements through either branched polymer chains or polymers without ionic end groups. These technologies will be addressed in a later section.

First, there are the copolymers made from two monomers of vinylidene fluoride (VF_2) and hexafluoropropene (HFP). These polymers are most often cured with bisphenol AF and a phosphonium salt. Copolymers are typically 65-66% fluorine by weight. Copolymers are divided further into subcategories of cure incorporated, molded goods grade, O-ring grade, and non-cure containing gum. Copolymers are the most widely used of the FKM types due to their good overall performance.

Fluoroelastomer Monomers



Vinylidene Fluoride (VF2)

Hexafluoropropylene (HFP)

Tetrafluoroethylene (TFE)

Perfluoromethylvinylether (PMVE)

Figure 3.

Next are the terpolymers. These polymers are composed of VF_2, HFP similar to a copolymer, but which also have a third monomer of tetrafluoroethylene (TFE). TFE is added to increase the fluorine content of the polymer to give the polymer better chemical and heat resistance than a copolymer. This can, however, result in poorer compression set and reduced low temperature sealing properties. Terpolymers are also most often cured with bisphenol AF and range in fluorine content from 67-70% by weight.

Terpolymers also are divided further into the subcategories of cure incorporated molded goods grade, O-ring grade, and non-cure containing gum. Terpolymers are often used in automotive fuel systems and non-metallic expansion joints.

Peroxide curable polymers are similar to terpolymers except a cure site monomer (CSM) is added to the polymer backbone. The CSM allows a radical to be formed by a peroxide and then cross linked by a co-agent. Peroxide curable FKMs typically range in fluorine content from 67-70% by weight. They offer better chemical resistance than corresponding terpolymers with the same fluorine percentage because the peroxide cure mechanism does not create unsaturations in the polymer backbone that is found in a bisphenol cured polymer.

FKM Type	Monomers	Curable by:	Recommended Curative
Copolymer	VF2, HFP	Amine, Bisphenol	Bisphenol
Terpolymer	VF2, HFP, TFE	Amine, Bisphenol	Bisphenol
Peroxide Curable	VF2, HFP, TFE, CSM	Amine, Bisphenol, Peroxide	Peroxide
Low Temperature	VF2, HFP, TFE, PMVE, CSM	Amine, Bisphenol, Peroxide	Peroxide

Figure 4.

Low temperature polymers are typically peroxide curable with an additional monomer of perfluoromethyvinyl ether (PMVE). The ether linkage in the backbone gives these polymers outstanding low temperature flexibility. They are divided by their temperature of retraction (TR 10) value.

Polymer Classification	First Division	Secondary Classification
Cure Incorporated	O-ring , Molded Goods (Cross link Density)	Viscosity/Molecular Weight Distribution, Cure Rates, Boding Promoters, Internal Process Aids
Gum Stock	Viscosity/Molecular Weight Distribution	Metal Bonding Promoters, Internal Process Aids

Figure 5.

Some grades do not fit neatly into the categories presented above and are considered specialty polymers. Examples are special low durometer polymers and base resistant polymers. Other grades use integrated fillers for unique physical properties or high purity applications.

Fluorine Content by Weight Can Be Misleading

Often the fluorine content of the polymer is expressed in percentage by weight for comparison purposes. Although this is a simple method of determining the general chemical resistance of a polymer, it must be used with caution. The addition of PMVE into the polymer backbone improves chemical resistance but reduces the fluorine percentage by weight. The oxygen in PMVE-containing polymers changes the fluorine percentage vs. polymers with only carbon, hydrogen, and fluorine. For this reason, the available hydrogen in a polymer is the most important factor in determining the polymer’s chemical resistance.

Fluoroelastomers Based on New Polymerization Technology

An FKM can be cross-linked by one of several cure systems. The most common is the bisphenol cure system. This cure system can be used with any polymer containing $VF_{2.}$ It includes most peroxide curable polymers but, due to its cost disadvantages, is not recommended. Bisphenol AF (BAF), a phosphonium salt, and an acid acceptor such as calcium hydroxide or magnesium oxide are required to complete the cure package. Bisphenol is the cross-linking structure, while the phosphonium salt is the accelerator. The quantity of BAF determines the cross-link density while the quantity of phosphonium salt changes the cure rate. The quantity and type of acid acceptor also determines the rate of reaction and cross-link density.

Cure System Comparison 1=Best			
	Diamine	**Bisphenol**	**Peroxide**
Control of Cure Rheology	3	1	2
Heat Resistance	3	1	2
Compression Set	3	1	2
Processing	3	1	2
Special Feature	FDA Applications, Bonding, Latex and Solutions	Most versatile in Cure Control	Best Chemical Resistance

Figure 6.

The amine cure system was the first cure system developed for FKMs. It requires the addition of a diamine and an acid acceptor. Typically 10-15 parts of low activity magnesia is added to the compound. The amine systems typically are used for FKM solutions for their good bonding characteristics. Amine systems are very scorchy and are very sticky during molding. Today compounds with amine systems are rare and in most cases considered obsolete.

The peroxide cure system is the most chemically resistant system. This system is used in high fluorine polymers and low temperature polymers. The polymer backbone must contain a CSM. An organic peroxide and co-agent are used to complete the cure. The peroxide generates a free radical which creates a bond between the co-agent and the polymer.

Tecnoflon HS

Tecnoflon HS is a patented technology which offers a dramatic reduction in post cure time. The technology revolves around a polymerization process that creates a polymer without ionic end groups.

Compression set resistance that normally required sixteen to twenty-four hours of post cure is now achieved in one or two hours. Tecnoflon HS compounds are compounded without calcium hydroxide, thereby eliminating associated processing problems. Unique properties for HS polymers include:

1. Fast cure rate
2. 1-2 hour post cure time
3. No mold fouling
4. Excellent scorch safety
5. Excellent compression set resistance
6. No calcium hydroxide

Tecnoflon P

New (first commercialized in 1997) Tecnoflon P grades have a branched structure. The branched polymer chain allows for a CSM to be placed at the end of each branch. When cured, the part is highly networked resulting in significant compression set resistance improvements. Other major advantages of this branching technology are:

1. Compound viscosity: The compound viscosity remains low even in highly filled compounds. The improved flow enables the injection molding of parts, a process previously not possible because of flow restrictions.

2. Mold release: Each chain end has a cure site which cannot react with the mold surface. The cure is very efficient in tying up most of the co-agent and peroxide.

3. Hot tear strength: The branched network greatly improves hot tear strength when combined with the outstanding mold release. This results in high molding yields and low scrap rates.

4. Fast cure cycles: The efficiency of the cure mechanism results in very fast cure cycles. Typical injection molding cycles are under one minute.

5. No or very short post cures: The efficiency of the cure mechanism and cure network gives new parts out of the mold outstanding properties. In many cases the part will meet specification without a post cure. For the most demanding applications, a short post cure up to four hours will optimize the physical properties. Longer post cures, sixteen to twenty-four hours, required by old technologies are not necessary as the physical properties are at their peak within two to four hours.

Compounding

Fillers

As a rule, most fillers used in other rubber formulations may be used in a FKM compound. However, the filler needs to be as chemically resistant and as thermally stable as the polymer.

Carbon Black

Carbon black is the filler of choice for most FKM formulations, specifically MT N-990 carbon black. MT N-990 offers the best overall physical properties and loading levels. N-990 builds viscosity less than other fillers thus allowing for greater flexibility in molding operations. Smaller particle carbon blacks may be used but in lower percentages of the formulation. Not only do smaller carbon blacks build durometer but they also retard the cure rate due to their acidic nature. Using N-330 over 10 phr seriously slows the cure rate and may result in an unusable compound.

Mineral Fillers

Clays, silicas, and other fillers may also be used. Wollastinite, precipitated silica, PTFE and barium sulfate are most commonly used in mineral filled compounds. Reasons to use mineral fillers include higher loading levels for better volume cost, colored compounds, FDA applications, and semiconductor applications. Clays and other minerals with waters of hydration tend to increase the cure rate of bisphenol cured compounds. Special care must be taken when using these fillers in injection molding operations as they provide less scorch safety and do not flow as well as carbon filled compounds.

Another issue often overlooked when compounding with mineral fillers is chemical resistance. Such an example would be compounding for acid resistance with a mineral filler that reacts in an acidic environment.

Pigments

Color compounds are limited in fluoroelastomers by the heat and chemical stability of the pigments. Many organic pigments will survive the initial curing process but will decompose during post cure. Many brown pigments will change to a pink or salmon color after post cure. The most common colors in addition to black are brown, red, green, blue, and white. The color of the uncured compound usually varies slightly from the cured and post cured part. There is a color shift in the polymer to a brown color in a compound without pigment. This change is a result of the acid generation during the cure and posture cycles.

It is often advisable in a colored compound to add a very small amount of carbon black to the formulation. This will darken the compound and help mask any contamination picked up in the mixing and molding process. In a mineral filled compound, pigments are loaded between 1 and 10 phr depending on the desired color of the article. Pigments tend to have a high specific gravity and should be used in the lowest level to give the best volume cost.

Process Aids

Process aids or plasticizers, as rule, should be used as little a possible. Carnauba wax has been historically used as the process aid of choice for fluoroelastomers but has been replaced in recent years by more advanced materials. When choosing a process aid the polymer type, milling, molding, and part shrinkage need to taken into consideration. In some cases, a process aid is added to the base polymer by the fluoroelastomer supplier. This may include dichloro diphenyl sulfone (DCDPS), fluorinated oils, and others. An additional amount added during compounding may help the milling characteristics and molding performance of the compound. Tecnoflon FPA 1, available from Solvay Solexis, is a fluorinated wax developed as a process aid which improves flow and mold release in FKMs and other elastomers.

Typical Standard Technology Bisphenol Incorporated, O-ring Compound (Copolymer, 75 Durometer)

Material	Parts
O-ring Grade Polymer	100
Calcium Hydroxide	6
Magnesium Oxide (High Activity)	3
MT N-990 Carbon Black	30
Process Aid	0.5

Figure 7.

Typical Tecnoflon HS Technology Bisphenol Incorporated, O-ring Compound (Co-polymer, 75 Durometer)	
Material	**Parts**
O-ring Grade Polymer	100
Magnesium Oxide (High Activity DE)	9
MT N-990 Carbon Black	35
Process Aid	0.5

Figure 8.

Typical Peroxide Curable Formulation (75 Durometer)	
Material	**Parts**
Peroxide Curable Polymer	100
Zinc Oxide	3
Varox DBPH-50 or Luperco 101XL	2.5
TAIC DLC A (75%)	3.0
MT N-990 Carbon Black	35
Process Aid	0.5

Figure 9.

Compounding for Special Applications

Compression Set Resistance

Compression set resistance is a critical physical property for sealing applications. In general, bisphenol cured copolymers offer the best overall compression set resistance of the FKM types. However, other FKM types do offer good compression set resistance for most applications. Once the type of FKM has been selected based on heat and fluid resistance requirements, the best compound for compression set can be determined. Usually higher molecular weight polymers provide better resistance than lower molecular weight polymers. Increasing the cross-link density of the cured compound and providing a proper post cure for the polymer also have dramatic effects on compression set. Fillers too, have an effect. The use of Austin black 325 (coal fines) in a compound will improve compression set dramatically although compromising processability.

Large Parts

Parts with a cross section over one-half inch in diameter should be considered carefully. Several problems can arise including fissuring and backrinding.

Fissuring is caused by the water vapor released from the cross-linking reaction in bisphenol cured compounds. The water vapor cannot escape from the part during post cure and consequently fissures the part during post cure. The addition of calcium oxide in the compound will act as a water scavenger and prevent the internal steam pressure from fissuring.

Back grinding is caused by the thermal expansion of the polymer and resulting flow through already cured material. Besides curing at a lower temperature the cure rate can be slowed by reducing the amount of accelerator or acid acceptor. In addition, a lower molecular weight polymer will also allow for better flow and lower internal mold pressures.

Metal Bonding

Metal bonding is easily accomplished with bisphenol and amine cured systems. The addition of mineral fills, calcium hydroxide, magnesium oxide, and calcium oxide will improve addition and the reaction with the adhesive. In general, compounds with higher loading levels adhere better than those with lower loading levels. Process aids should be kept to the bare minimum as they will foul the bonding surface. Some polymers contain metal bonding promoters incorporated by the fluoroelastomer manufacturer. If possible, start with one of these polymers as the basis of the compound.

Peroxide cured polymers may also be bonded but special compounding is usually required. For difficult to bond compounds, a tie layer may be used between the compound and the adhesive. The tie layer usually consists of a specially compounded FKM dissolved in methyl ethyl ketone (MEK) then applied to the bonding substrate and allowed to dry.

Abrasion Resistance

FKMs are less abrasion resistant when compared to other elastomers such as natural rubber. However, FKMs are frequently used in dynamic seals. Compounding with polytetrafluoroethylene (PTFE) micro powders, molybdenum disulfide, or graphite will increase abrasion resistance and extend the life of a dynamic seal. Steam resistant peroxide cured FKMs are the clear choice for applications exposed to steam. Peroxide curable polymers do not have the metal oxides of bisphenol cured compounds which absorb water and cause large volume swells and physical property losses. Steam resistance is also improved by increasing the fluorine content of the polymer. The first choice in polymers in this case would be a 70% fluorine peroxide curable FKM such as Tecnoflon P 459 or P 959.

Within peroxide cured systems, the acid acceptor type and quantity must be carefully selected. Litharge, a lead oxide, contributes less to volume swell and property loss than zinc oxide. Litharge should be considered carefully because of its environmental consequences. Since lead usage is increasingly scrutinized by environmental regulations, it may be best not to use it at all. Curing without an acid acceptor is possible and will give similar or better resistance than lead oxide.

Perfluoroelastomers also offer excellent steam resistance. They are especially useful in high purity water applications and in environments containing mixtures of steam and aggressive chemicals. Tecnoflon PFR 94 and PFR 5910M are well suited to these applications.

Food Grade

Most manufacturers’ polymer gums qualify as food grade, but the cure packages and fillers determine if a compound is suitable in a food or edible oil application. Compounders should consult FDA CFR 177.2600 and their polymer supplier before compounding. Barium sulfate and titanium dioxide are commonly used as fillers in these applications.

Steam Resistant Formulations:	**A**	**B**	**C**
Tecnoflon P459	100	100	100
Varox DBPH-50	2.5	2.5	2.5
TAIC DLC-A	3	3	3
Zinc Oxide	0	5	0
Litharge	0	0	5
N-990 black	40	40	40
Struktol WS 280, paste	0.5	0.5	0.5
Physical properties: press cure: 10' @ 177°C post cure: 4 h @ 230°C			
Hardness Shore A, pts.	83	83	85
Tensile Strength, psi	2723	2799	2810
Elongation, %	222	223	225
Modulus @ 100%, psi	1060	1065	1158
Fluid Resistance, ASTM D471 water, 70h @ 200°C: O-rings			
Change in Durometer, pts.	-9	-12	-12
Change in Tensile, %	-20	-42	-45
Change in Elongation, %	36	7	37
Change in Modulus @ 100%, %	-38	-37	-44
Volume Change, %	8	15	7
Fluid Resistance, ASTM D471, steam, 22h @ 200°C: O-rings			
Change in Durometer, pts.	-9	-9	-9
Change in Tensile, %	-37	-54	-53
Change in Elongation, %	61	38	71
Change in Modulus @ 100%	-33	-32	-38
Volume Change, %	3	4	2

Figure 10.

Permeation Resistance

FKMs have low fuel permeation rates when compared to hydrocarbon-based elastomers. A quick test to determine relative permeation resistance can be done by a volume swell test. A polymer with lower volume swell in a given fluid generally corresponds to better permeation resistance than a polymer with a high volume swell. The best permeation resistant FKMs are the 70% fluorine peroxide curable polymers.

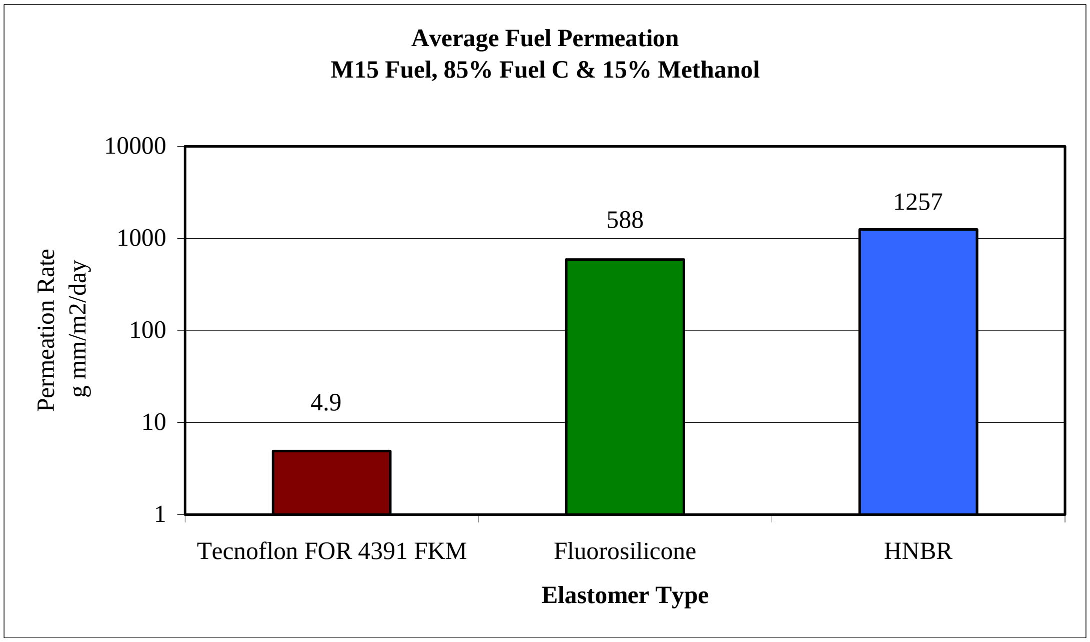


Figure 11.

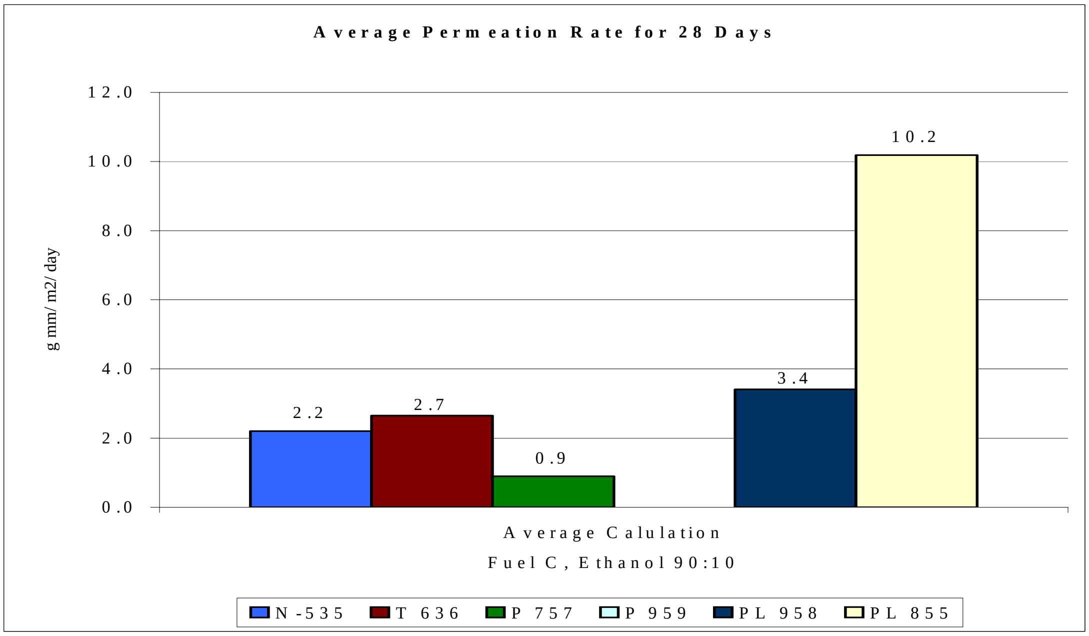


Figure 12.

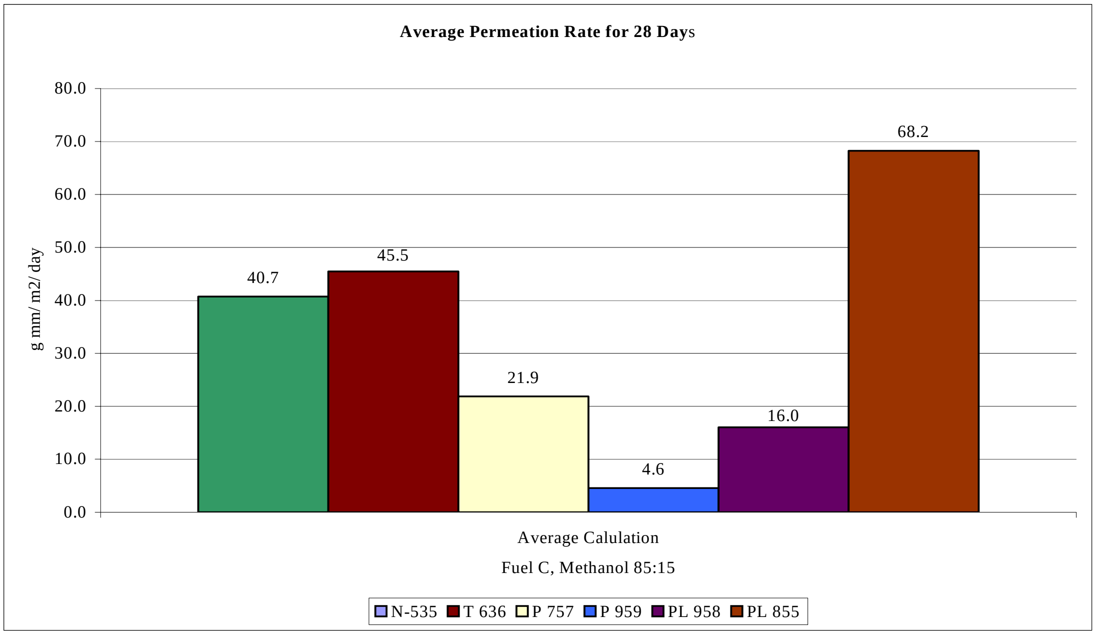


Figure 13.

Low Temperature Sealing

Low temperature sealing is accomplished by selecting the correct grade of polymer to meet the temperature range of the finished rubber article. The industry standard for determining the ability of an elastomer to seal, especially in a dynamic application, is the 10% Temperature of Retraction (TR-10). Standard bisphenol cured copolymer FKMs have a TR-10 value of approximately –18°C (-1°F). As a rule, as the fluorine percentage of the polymer increases, the low temperature flexibility decreases. Special grades of low temperature bisphenol terpolymers have been developed to have TR-10s of –19°C and –21°C respectively.

The addition of PMVE into the polymer backbone allows for greater low temperature flexibility. Special grades of peroxide cured FKMs have been developed for –24, -26, -29, -30ºC. As in the case of the bisphenol cured elastomers, the fluid resistance of the polymer tends to decrease as the low temperature performance increases.

Special care should be taken when a specification requires a brittle point. The brittle point moves counter to the TR-10 with respect to the fluorine level in VF2, HFP, TFE co and terpolymers.

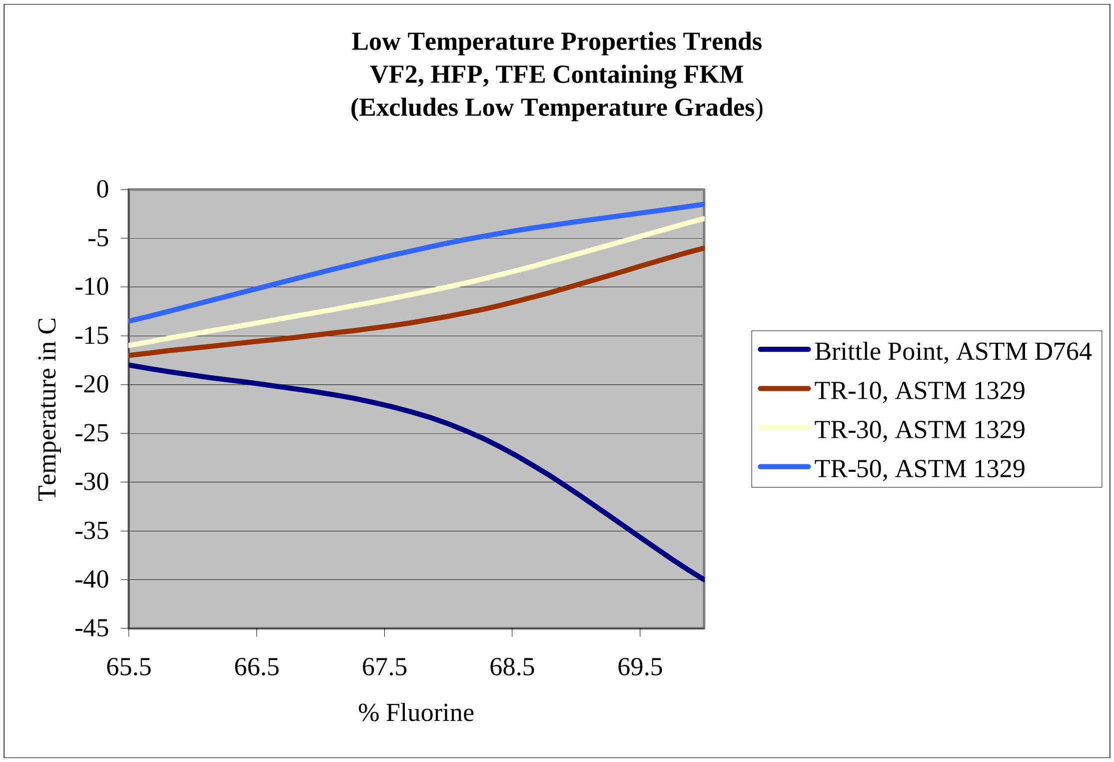


Figure 14.

Tecnoflon Low Temperature Grades			
Grades	**Fluorine Content**	**TR-10**	**Cure Type**
T 636	66	-19	Bisphenol
L 636	65	-21	Bisphenol
PL 458	67	-24	Peroxide
PL 958	67	-24	Peroxide
PL 956	66	-26	Peroxide
PL 557	66	-29	Peroxide
PL 455	65	-30	Peroxide
PL 855	65	-30	Peroxide

Figure 15.

Low Durometer

Fluoroelastomers typically cannot be compounded less than about 55 Shore A durometer. Tecnoflon FOR LHF is unique in the marketplace in that it can be compounded to a Shore A of 45.

If another grade is chosen, the best way to achieve the lowest possible durometer is to choose a low molecular weight polymer with a low a level of curatives and fillers. Tecnoflon HS is particularly well suited for 50 Shore A applications.

Processing

Mixing

The fluoroelastomer polymer sold by the major manufacturers cannot be used in its raw state. It must be mixed with other materials before it can be usefully processed into a finished part or seal. Two methods are used to mix the polymer with the additives. One is the internal mixer and the other is the open mill.

The internal mixer is a machine that contains two intermeshing rotors which rotate to combine the polymer with the additives. This process is much faster that the alternate method of open mill mixing. Two problems associated with internal mixers is a constraint on batch size and the possibility of contamination from previous mixes. To properly mix a compound, the mixer must be filled to a certain volume so that the milling ram can exert a downward force to create shear and keep the mix in the rotors. The other problem is contamination. Mixers used for sulfur cure elastomers must be thoroughly cleaned before use with a fluoroelastomer. Even the smallest amount of sulfur contamination will poison the cure and ruin the FKM batch. In addition, it is difficult to run colored compounds in a mixer that also mixes carbon black containing batches and achieve uniform color.

Internal Mixing Parameters	
Mix Time	3-8 minutes
Compound Temp	90 –110^{o}C
Premix Dry Materials	
Thoroughly Clean Mixer	Avoid Sulfur Contamination

Figure 16.

An open mill will do an excellent job mixing fluoroelastomers. Disadvantages of mixing on an open mill are intensive time and labor. However, internal mixers provide better batch size and contamination control.

Open Mill Mixing	
Premix Dry Materials	
Roll Temperature	< 90^{o}C, Use Chilled Water Through Mill Rolls

Figure 17.

Milling

Upon completion of mixing in an internal mixer, the batch must be mixed on a rubber mill for several minutes to ensure cross blending of all the ingredients and to sheet the compound for cooling rapid. It is recommended that a batch milled twice ensures proper dispersion of the raw materials and breakdown of agglomerations.

A typical sequence is as follows:

1. Mixer
2. Mill
3. Cool-down
4. Remill
5. Cool-down
6. Package (slabs or strips)

Storage of Mixed FKM Compound

Compounds based on Tecnoflon FKM, like those based on other elastomers, are subject to a viscosity increase and reduction in scorch time as the compounds age. In addition to heat, the compounds are sensitive to humidity.

Mixed stock should be kept in cool, dry storage. Refrigeration is not required. However, humidity control is recommended. If the stock is refrigerated, then it should be removed from cold storage at least four hours prior to processing. All condensation must be removed by compressed air or by wiping with an absorbent cloth. Moisture in the compound will show itself in the form of small blisters on molded parts.

At temperatures below 30°C (85ºF) at 50% relative humidity, the mixed compound should have a shelf life of at least six months. Converters should refer to the manufacturer’s recommendations to ensure satisfactory shelf life and processing performance.

Pre-forming

The next step of processing FKMs is pre-forming. This is the shaping of the uncured material to enable further processing. Several methods are typically used including extrusion (hot and cold feed), hydraulic ram extrusion, sheeting, stripping, calendering and cutting.

Hydraulic Extruder	
Temperature	
Compound	80-90°C
Barrel	60-80°C
Head	70-100°C

Figure 18.

Cold Feed Extruder	
Temperatures	
Feed Box	15-30°C
1st Zone	55-65°C
2nd Zone	65-85°C
Head/Die	75-100°C
Screw	55-65°C

Figure 19.

Molding

Unlike other elastomers, fluoroelastomers must be cured under pressure in the form of a mold or autoclave to prevent the formation of bubbles or sponge. Hot air tunnels and microwaves cannot be used for curing unless they are pressurized. Molding either by compression, transfer, injection, or autoclave curing are the most common methods used for commercial processing.

Compression Molding

Compression molding is the oldest and most common form of molding of FKMs. Although injection molding is very popular in Europe, processors in the United States still rely heavily on compression molding. Molding temperatures range from 160°C to 200°C (320˚F to 390˚F) with larger parts being molded cooler to prevent backrinding.

Transfer Molding

A medium viscosity polymer is recommended. A careful consideration of cure rate is important to ensure scorch safety. Mold temperatures vary depending on the part. A temperature range of 160°C to 177°C (320˚F to 350˚F) is a good starting point.

Injection Molding

Injection molding is the most demanding molding process. The injection molding grade selected should have a molecular weight distribution to achieve the best flow and good scorch safety with a very steep cure rate. Molding fouling must be minimized by using formulations minimizing process aids and metal oxides.

Extrusion

Extrusion of FKMs is used to form extruded shapes, tubing, O-ring cord, and compression molding pre-forms. Extrusion parameters vary according to particular machines and tooling set ups so the fine tuning of each part is required. A starting set point of 66°C (150˚F) for the head and 93°C (200˚F) for the die will probably provide a smooth extrudate. Unlike other elastomers, FKM extrusions must be autoclaved cured. The release of water in the bisphenol cure mechanism creates foam and bubbles in the extrudates. Peroxide curable polymers are less susceptible to foaming due to the different cure mechanism but also tend to bubble without adequate pressure. Since autoclaves heat somewhat more slowly, the extrudate has a tendency to flatten or deform where the part touches the autoclave rack. Choosing the right polymer for its molecular weight and cure speed is the key to minimizing flattening. A delicate balance between molecular weigh of the polymer and the extrudability of the polymer must be achieved to create a smooth extrudate while minimizing deformation during cure.

Post Cure

Fluoroelastomers are improved by a post cure following the molding operation. Post cures complete the cure, burn out impurities and process aids, and create filler polymer interactions. The physical property influenced the most by a post cure is the compression set resistance. A post cure typically increases the tensile strength and modulus while reducing the ultimate elongation. A rise in durometer by several points is also expected

Not all polymers types require the same post cure time or temperature to maximize their performance. Older polymer types require lengthy post cures of sixteen to twenty-four hours. Newer polymers have been designed to be more efficient to maximize their performance with a few hours. This technology is most easily demonstrated on Solvay Solexis’ newest peroxide curable FKMs and Tecnoflon HS grade bisphenol cured copolymers. Depending on the end use of the part and specification, it may be possible to eliminate a post cure.

Bisphenol cured FKMs are typically post cured at 250ºC (482°F) while peroxide cured FKMs are typically post cured at 230ºC (446°F). Large parts may require a step post cure or a cure at a lower temperature to prevent fissuring.

Conclusion

Fluoroelastomers can withstand various hostile environments. The polymer selection and compounding ingredients should be considered carefully for each application. New polymer technologies are continually entering the market to improve processing speeds, efficiency, molding properties, physical properties, fluid, and heat resistance. For new projects or to improve an existing process, the Solvay Solexis technical team can provide the most suitable polymer technologies and compounding advice.

Appendix 1

Common Reference Fuels			
Reference:	**Name:**	**Composition**	**Percentage by Volume**
ASTM D 471	Reference Fuel A	Iso-Octane	100
	Reference Fuel B	Iso-Octane	70
		Toluene	30
	Reference Fuel C	Iso-Octane	50
		Toluene	50
	Reference Fuel D	Iso-Octane	60
		Toluene	40
	Reference Fuel E	Toluene	100
	Reference Fuel F	Grade #2 Diesel Fuel	100
	Reference Fuel G	Reference Fuel D	85
		Ethanol	15
	Reference Fuel H	Reference Fuel C	85
		Ethanol	15
	Reference Fuel I	Reference Fuel C	85
		Methanol	15
	Reference Fuel K	Reference Fuel C	15
		Methanol	85
DIN 51 604	FAM A	Toluene	50
		Iso-Octane	30
		Di-Isobutylene (2,4,4,-Trimethyl 1-Pentene)	15
		Ethanol	5
	FAM B	FAM A	84.5

Common Reference Fuels (continued)			
Reference:	**Name:**	**Composition**	**Percentage by Volume**
		Methanol	15
		Water	0.5
	FAM C	FAM A	40
		Methanol	58
		Water	2
AZ 105-01	Ford Base Fuel	Reference Fuel C	80
		Methanol	15
		T Butyl Alcohol (2-Methyl Propan-2-ol)	5
	PN 90	Ford Base Fuel	97.76
		70% t Butyl Hydroperoxide	1.24
		Copper Ion Solution	1
	PN 180	Ford Base Fuel	96.52
		70% t Butyl Hydroperoxide	2.48
		Copper Ion Solution	1

Appendix 2

Common ASTM Test Standards For Rubber	
ASTM Standard	**Description**
D 395	Compression Set
D 412	Stress Strain
D 429	Adhesion
D 471	Fluid Resistance
D 573	Heat Age
D 624	Tear Strength
D 1329	Low Temperature
D 1414	O-rings
D 1646	Mooney Viscometer
D 2000	Rubber Classification System
D 2084	ODR
D 2137	Brittleness
D 2240	Durometer
D 3182	Practice for Mixing and Molding

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