

Fluorine-Containing Elastomers

Introduction

Fluoroolefin history began in 1892 with the work of F. Swarts, a Belgian chemist and the well-known Swarts reaction named after him. This reaction led to the development of fluoroalkanes, the precursors of fluoroalkenes, fluoroalkenes in turn led to halogenated refrigerants. Volume production of these refrigerant gases offered a readily available volume source of monomers necessary for the production of today's fluoroelastomers with the actual birth of the fluoroelastomer industry in the early 1950's. The subsequent dynamic growth of the industry is very indicative of the commercial significance of these premium priced elastomers. This chapter might appear to have an undue level of depth but for good reason, suppliers' literature is often deficient in some areas of information necessary for the long-term service, i.e. some of these elastomers are capable of surviving.

Fluoroelastomer Development

The substitution of fluorine for a hydrogen on a carbon-backbone macromolecule creates a unique class of rubbers typically referred to as fluoroelastomers. The chemistry is straightforward: a hydrogen atom-H (atomic mass-1, atomic radius-0.12 nm) is replaced by a fluorine atom-F (atomic mass-19, atom radius-0.135 nm). Hydrocarbon rubbers (hydrogen and carbon) are classified as nonpolar, however, the substitution with fluorine creates polar molecules. Reference to the periodic chart helps explain the difference in polarity. Hydrogen is a Group I element where electrophilic reactions (electron pair acceptor-EPA) or acidic reactions dominate. Whereas fluorine, a Group VII element, is on the opposite side of the periodic chart where nucleophilic reactions (electron-pair donor-EPD) or basic reactions dominate. The measure of electronegativity or electron acceptance is 2.2 for hydrogen and 4.0 (the maximum value) for fluorine on the Flory Electronegativity Scale. A review of bond strengths helps explain, in subsequent discussion, the changes in properties achieved through the fluorine substitution.

Polar Bond Strength

Bond strengths, or more correctly homolytic bond dissociation energy (BDE) as measured on a simple alkane-methane and a halogen (fluorine, chlorine, bromine, iodine) substituted methane are revealing.

CH ₃ -H	435 kJ/mol
CH ₃ -F	451 kJ/mol
CH ₃ -Cl	351 kJ/mol
CH ₃ -Br	293 kJ/mol
CH ₃ -I	234 kJ/mol

It is apparent that bond dissociation energies establish basic parameters for both elastomer thermal stability and ease of abstraction for crosslink site development.

Fluoroelastomer Classifications

ASTM D1418 – “Standard Practice for Rubber and Rubber Latices – Nomenclature” offers a convenient and preferred ASTM categorization for fluoroelastomers by listing three (3) categories (FKM, FFKM, and FEPM) and their general description. Logically these categories should define the classification of the monomers used in the polymerization. Although not specifically designated, they also define the ultimate service application. D1418-98, as all ASTM specifications, is subject to revision, approval and/or reapproval. The following nomenclature might be logical for subsequent revisions.

FKM, is the largest category (80+%) of fluoroelastomer. All FKM designated elastomers contain vinylidene fluoride (VF₂), a disubstituted monomer. Due to the growth of this category a more logical D1418 description might be:

“FKM – Fluoro rubber of the polymethylene type that utilizes vinylidene fluoride as a comonomer and have substituent fluoro, alkyl, perfluoroalkyl or perfluoroalkoxy groups in the polymer chain, with or without a curesite monomer”.

There are currently five (5) logical FKM category elastomers currently differentiated only by trademarks. They might now be classified as the following FKM types:

- Type 1. Dipolymer of hexafluoropropylene and vinylidene fluoride
- Type 2. Terpolymer of tetrafluoroethylene, hexafluoropropylene and vinylidene fluoride
- 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, ethylene, a fluorinated vinyl ether and vinylidene fluoride

2) The current FFKM designation “Perfluoro rubbers of the polymethylene type having all substituent groups on the polymer chain either fluoro, perfluoroalkyl, or perfluoroalkoxy groups” needs no change.

3) The third category, FEPM (originally designated for “Copolymer of tetrafluoroethylene and propylene”), requires updating for the addition of new elastomers

suitable for similar service. The implied service suitability defined by the tetrafluoroethylene and propylene monomers would be adequately defined by the following nomenclature change:

“FEPM-a fluoro rubber of the polymethylene type containing one or more of the monomeric alkyl, perfluoroalkyl, and/or perfluoroalkoxy groups with or without a curesite monomer (having a reactive pendant group).”

Fluoroelastomer Categories

Using the ASTD 1418 background, we can simply state that fluoroelastomers are available in three compositionally distinct categories based on polymerization of two or more specific types of monomers:

Monomer Category

1. Nonsubstituted (hydrocarbon) alkene monomers (ethylene-E propylene-P).
2. Partially substituted (hydrofluoro) alkene monomers (vinylidene fluoride-VF₂).
3. Fully substituted (perfluoro) alkene monomers (tetrafluoroethylene-TFE, hexafluoropropylene-HFP, perfluoromethyl vinyl ether-PMVE).

Referring back to the various FKM classifications, we can further differentiate specific applications:

FKM Category

- Type 1: General purpose, best balance of overall properties. Typical 66 weight percent of fluorine.
- Type 2: Higher heat resistance, best aromatic solvent resistance of the VF₂ containing fluoroelastomers. Typical 68 and 69 ½ weight percent fluorine.
- Type 3: Improved low-temperature performance, higher cost. Typical 62 and 68 weight percent fluorine.
- Type 4: Improved base resistance, higher swell in hydrocarbons, decreased low-temperature performance. Typical 67 weight percent fluorine.
- Type 5: Improved base resistance, low swell in hydrocarbons, improved low-temperature performance.

FFKM Category

These elastomers, correctly defined as perfluoroelastomers (totally fluorinated-no hydrogens) have outstanding fluid resistance, base-resistance, dielectric properties and high temperature resistance. The major market (80%) is essentially solvent resistant applications. Aerospace applications range from oxidizer resistant components and both commercial and military jet engine seals operating in a sustained high temperature environment. Originally introduced by Dupont (Kalrez[®]), in the 1970's, additional suppliers are Daikin (Japan-1980's) and Ausimont (Italy-1990's).

FEPM Category

The original developer (Dupont-1960's) never commercialized the elastomer, a copolymer of propylene and tetrafluoroethylene due to lack of market interest. Reintroduced (Asahi Glass Co.-1970's), the elastomer found a specific niche in the emerging high-temperature "sour" oil and gas production environment operating continuously at temperatures in excess of 200°C in the presence of hydrocarbons, carbon dioxide, hydrogen sulfide and brines. The addition of very basic inhibitors (amines) during hydrocarbon production and the presence of metal halides in completion fluids (ranging from very weak to very strong Lewis acids, as well as, very basic chemicals) have made this category of fluoroelastomers the material of necessity in this environment. The fundamental properties of propylene-tetrafluoroethylene rubber are a function of the characteristic properties of the non-substituted alkene and a totally fluorinated alkene. Hence other monomer combinations offer similar properties with possible enhancements desirable i.e.; lower swell in lighter and aromatic hydrocarbons and improved low-temperature properties. In summary, this category of elastomers is unique in both aqueous and nonaqueous electrolytes, which include engine coolants and highly stabilized lubricants. Along with the FFKM category it is suitable for service in all classes of petroleum based hydraulic fluids, di and polyesters, phosphate ester and silicic acid ester fluids.

Service Fluids Resistance

The major usage of fluoroelastomers is in automotive applications. The increasing environmental demands of service applications have produced some unique challenges as detailed.

Fuels: Gasoline, once a relatively simple mixture of aliphatic and aromatic hydrocarbons now require oxygenates (MTBE, methanol, ethanol and octanol) to reduce the NO_x potential.

These mixtures are now a “mixed solvent” system of polar and non-polar components, a seal designer’s nightmare. The lowest volume changes are achieved by the FKM Class 2, 69 ½ weight percent fluorine class. If improved low temperature performance is required, FKM Type 3 fluoroelastomers might be considered (at a higher cost).

Engine Lubricating Oils: Demands for higher performance engines has raised the bulk oil operating temperatures. To meet the new SAE requirements, lubricant suppliers are using increasingly aggressive stabilizer packages. The ASTM reference material, is ASTM Service Fluid 105 representing SAE 5W30. Polymer suppliers feel this standard is too aggressive and point out that “aerated” engine oil is far less aggressive. This is understandable since the additive packages are designed to scavenge oxygen hence the lubricant stability is being rapidly diminished. The automotive manufacturers still recommend 3000 mile oil changes (which represents 60-80 hours of driving time) so the stabilizer package in real life is being renewed on a regular basis. The effect the stabilizers have on fluoroelastomers is discussed in more detail in the discussion “Aqueous and Nonaqueous Electrolytes.

Crosslinking Theory

The process of curing (crosslinking) creates a three-dimensional structure that makes the elastomer suitable for long-term mechanical service under a sustained load (stress) or constant deformation (strain). The two services are the typical initial requirements for shock and vibration control or sealing. Invariably the crosslinks themselves are often the most vulnerable component of the cured elastomer. By reviewing the crosslinking mechanism from both a physical (mechanical) perspective and its chemical structure, we often get our first indications of long-term serviceability. In order to crosslink fluoroelastomers, there are

two distinct halogen elimination reactions that are used to develop crosslinking sites in hydrofluorocarbon elastomers:

1. E2 Mechanism - the simultaneous departure of hydrogen and the adjacent fluorine initiated by a nucleophile (base). This is the logical route reaction for creating the crosslink site (a double bond in the backbone) for the vinylidene fluoride containing elastomers.

2. E1 Mechanism - normally operates without a base. The crosslink initiating mechanism is ionization provided by an electrophile (peroxide radical). The specific location is a cure-site monomer (CSM) having an iodine or bromine substitution that is readily displaced by the peroxide radical. In the case of perfluoroelastomers, there are several suitable cure-site monomers having a reactive pendant group thus leaving the backbone intact, which in turn improves the long-term heat resistance. After developing the crosslink site, the different chemical mechanisms for each cure route use the following different reactions
 - a. Addition reaction – diamine crosslinks
 - b. Aromatic nucleophilic substitution reaction – dihydroxy crosslinks
 - c. ENE reaction – triazine crosslinks

Keep in mind the first two reactions are IONIC, and the third FREE RADICAL.

Crosslinking Chemistry

Diamine Cures

The original crosslinking chemistry used a (CO₂) blocked diamine, hexamethylene diamine carbamate (HMDAC). The very basic character of any amine initiates dehydrofluorination at a vinylidene fluoride (VF₂) site, now followed by an amine addition (crosslink). The subsequent hydrogen fluoride (HF) molecule reacts with magnesium oxide (a compounding ingredient) rearranging to form magnesium fluoride and water. The water is loosely bound as magnesium hydroxide. Thus each crosslink is accompanied by one mole of water and one mole of carbon dioxide. This is essentially an equilibrium reaction until the water is driven off by an extended high temperature postcure. The amine cure system still enjoys some popularity as it enhances rubber-to-metal bonding and the hexamethylene crosslink is mechanically mobile offering interesting dynamic properties. Note: the detailed description of this crosslinking mechanism is designed to educate the reader about the relationship between any basic environment and the vinylidene fluoride component of the FKM class of fluoroelastomers.

Dihydroxy Cures

The dihydroxy cure or Bisphenol AF system was commercialized in the 1970's and became an immediate success. The system offered dramatically improved compression-set resistance, excellent heat stability and greatly improved processing safety. Hydrolytic (water) stability was also improved. Again, the vinylidene fluoride presence was necessary to develop a crosslinking site. For hydrocarbon service, it is the preferred cure system.

Triazine-Peroxide Cures

Triazine (peroxide) crosslinking occurs at specific sites available on the curesite monomer (CSM). The cure-site monomer and curing mechanism was originally developed for an improved low-temperature fluoroelastomer based on vinylidene fluoride (VF₂) and perfluoromethyl vinyl ether (PMVE). The very acidic VF₂ and the ionic cure mechanisms (diamine and BPAF) create cleavage of the trifluoroalkoxy group on the PMVE resulting in backbone cleavage, and a perfluoromethanol by product. The addition of the curesite

monomer allows an orderly crosslinking (electrophilic as opposed to nucleophilic) process whereby the triazine structure becomes the crosslink.

Compounding Guidelines

Typical fluoroelastomer formulations utilizing the different cure mechanisms consist of the following (all quantities listed in parts per hundred parts rubber, phr).

Vinylidene Fluoride Types-Diamine Cure

Diamine crosslinker	1-3
Inorganic base: MgO, lead salts	15
Filler: carbon black	15-60

Vinylidene Fluoride Types-Bisphenol Cure

Bisphenol crosslinker	1-3
Quaternary phosphonium accelerator	0.25-1
Inorganic bases	
Ca(OH) ₂	3-6
MgO	3-6
Filler: carbon black	15-60

Cure-Site Monomer-Triazine (Peroxide) Cure

Triazine crosslinker	3-9
Organic peroxide	2-6
Inorganic base: ZnO	3-6
Filler: carbon black	15-60

Mixing can be done on both open mill and internal mixers. The high Mooney elastomers have rapid heat-buildup tendencies and should be treated accordingly.

Process aids, both proprietary and generic, are widely available. Typically, materials such as paraffin, low-molecular-weight polyethylene, and waxes are commonly utilized. More complex and expensive process aids are offered; however, there is no outstanding candidate. Fillers typically are the N990 thermal blacks. These blacks offer reasonable reinforcing characteristics, with the economy of higher loadings and lower attendant hardness increases. Furnace blacks ranging from N100 to N700 types are used to develop specific properties for oil-field applications. Non-black fillers should be utilized with great caution because of the rigorous environments fluoroelastomers are subject to. Briggs et al. (1) should be reviewed before considering non-black fillers. In addition, aqueous testing should be performed at the pH anticipated in actual service. Some non-black fillers and compounding ingredients are very specific in some instances to pH variation.

Plasticizers are generally ineffective due to their lack of permanence. The efficiency of a plasticizer (which must be thermodynamically soluble) is a function of the molecular weight: the lower the value, the higher the efficiency. This is also true of the plasticizer's volatility: increasing molecular weight, decreasing volatility. The 200°C postcure tends to volatilize most plasticizers during the postcure process.

8.6 Fluorine-Containing Elastomer Blends

Blends of other elastomers have not proven successful due to phase incompatibility. Polyacrylate elastomers have occasionally been utilized to reduce compound costs in diamine cured formulations. These blends offer no improvements in heat or fluid resistance and, more important, they decrease critical performance.

Aqueous and Nonaqueous Electrolytes

Hildebrand (2) in his classic text "Solubility of Nonelectrolytes" was very specific by excluding electrolytes. The concept of "likes dissolving likes", essentially elastomer compatibility is specific to nonelectrolytes. Electrolytes by definition are chemical compounds which when molten or dissolved in certain solvents, usually water, will conduct an electric current. The idea of a dissolved electrolyte and its solvent was highly controversial until the 1900's when the hydration of ions was proven indisputably. G. N.

Lewis in the 1920's proposed the acid-base definitions based on hydration ultimately leading to the quantum mechanical definitions summarized as: Acid (which can be a molecule, ion or nonmolecular solid), which can accept a share in a pair of electrons during a reaction. Now referred to as an electron pair acceptor or EPA. Conversely, a Base (molecule, ion or nonmolecular solid) which can donate a share in a pair of electrons during a reaction, now referred to as an electron pair donor or EPD.

The previous discussion, although tedious, is necessary to understand fluoroelastomers in the aqueous and nonaqueous electrolytes commonly encountered under the guise of engine coolants, stabilized lubricants and fluids commonly used in energy production to prevent corrosion. A chemical reaction occurs simplistically thru a gain or loss of electrons. Jensen (3) notes "all degrees of electron donation are possible, ranging from nearly zero in the case of weak (but specific) intermolecular attractions and idealized ion associations, to complete transfer of one or more electrons "(redox)". In summary, the effect on specific elastomers with a vulnerable monomer can range slow to rapid based on time-temperature relationships. The inevitable is it will occur and is predictable by the monomer chemistry whose identity does not get disguised by the polymerization process. Specific to fluoroelastomers, alkanes, fully substituted perfluoroalkanes and perfluoroalkoxy alkanes are very stable in electrolytes. Partially substituted alkanes (vinylidene fluoride-VF₂) are vulnerable to dehydrofluorination by well-defined chemistry, a path normally used in crosslinking VF₂ containing fluoropolymers with BPAF. Harwood (4) notes this dehydrofluorination process leaves a very weak double bond in the elastomer chain leading to backbone cleavage. He further notes much damage is done by a small amount of chain cleavage – 1% breakage reduces the degree of polymerization to 100 (from the original of 10,000 molecular weight for a fluoroelastomer). Thus, a VF₂ containing fluoroelastomer should be used with caution in the aqueous and nonaqueous electrolyte environment.

Crosslink Vulnerability

Crosslinks, the product of vulcanization, are typically the weak links in most molded rubber products. The comments in "Crosslinking Chemistry" offer clues to long-term stability which are now summarized.

Diamine Cures, still used for some dynamic applications are vulnerable to water with the diamine capable of being rehydrated leading to crosslink scission.

Dihydroxy Cures, the most widely used system is the most thermally stable. In long-term (1000 hrs +) aqueous environment, the dihydroxy oxygen (ether) linkage can cleave to create an olefin via a hydro-alkoxy-elimination leaving residual weak double bond in the backbone.

Peroxide-triazine Cures, are not as thermally stable as the dihydroxy system. The triazine ring can dissociate at high temperatures but is the preferred-system for aqueous and nonaqueous electrolytes.

Low-Temperature Properties

Fluoroelastomers in general have low temperature properties dictated by two factors: the size of the fluorine atom and the substituent fluorocarbon molecules (trifluoro and trifluoroalkoxy groups) and the various intermolecular molecular forces that come into play due to fluorine's high electronegativity.

Although the fluorine molecule is compact, a fully fluorine substituted carbon-carbon backbone (polytetrafluoroethylene) polymer is rod-like. To accommodate the larger size fluorine (as opposed to a hydrogen) the fluorines must be staggered giving the appearance of a slow spiral, a 180° turn for every 13-15 main chain carbons. This precondition eliminates any possibility of a rubbery state. The smaller hydrogen atom (ethylene, propylene, etc.), or a partially substituted alkyl (vinylidene fluoride) create room for chain (backbone) mobility. The presence of a bulky branch group (methyl, trifluoromethyl or perfluoroalkoxy) causes the polymerization to create the "random walk" chain configuration that is necessary for a "rubbery" elastomer. The reported low temperature properties of various fluoroelastomers creates much confusion, consider the data in Table I from Dupont (5).

Table I
Low Temperature Properties:

	FKM (1)	FKM (2)	FKM (3)	FEPM ⁽¹⁾	FEPM ⁽²⁾
TR – 10 (°C)	-17	-14	-7	+2	-11
T _g (DSC)	-15	-14	-7	+3	-11
Brittle Pt.	(ASTM D2137, Pass-°C)				
	-20	-35	-48	-58	-34

(1) Copolymer

(2) Terpolymer

Table I are low temperature properties without the consideration of time. Elastomers are a thermodynamic model, in actuality a legitimate physical description has to encompass the physical parameters of work (stress/strain) temperature and time. By the nature of rubber there can be no true definition of a static application – in deforming rubber, energy is stored waiting to be released. The so-called viscoelastic nature of elastomers is typically modeled with a spring to simulate the elastic force, whereby stress is in phase with the deforming force and directly proportional to strain (Hooke's Law). The viscous response (90° out of phase) modeled using a dashpot (similar to a car shock absorber) and is time-temperature dependent non-recoverable energy (a source of heat). This response of rubber to a deformation and its subsequent elastic recovery rate can be predicted by a lab instrument referred to as a dynamic mechanical rheological thermal analyzer (DMRT). Consider now looking at two fluoroelastomer categories using DMRT: FKM Type 1 and FEPM copolymer of equivalent Shore A durometer hardness are subjected to a dynamic loading (automobile traveling at 45 mph) of 63 radians/sec or 10 Hz.

Table II

Dynamic Data

Fluoroelastomer		E*, Complex Dynamic Modulus (MPa)	Tan δ
FKM Type I	20°C	18.4	0.50
	100°C	10	0.08
FEPM (Copolymer)	20°C	45.4	1.34
	100°C	8.4	0.15

A quick analysis of the tan δ data would suggest that the FKM Class I material has pronounced damping at 20°C and very resilient at 100°C. E* or “apparent” engineering modulus indicates some reduction in load-bearing capabilities. FEPM copolymer data indicates very strong damping (slow elastic recovery) at 20°C as well as a pronounced reaction to lower temperature (E*). At 100°C the complex modulus is similar to the FKM but the tan δ value indicates damping (slow elastic recovery rate).

DMRT data can be extremely revealing; consider now a comparison of two equal hardness fluoroelastomers after aging for 1000 hrs at 150°C in ASTM SF-105 Test Fluid (SAE 5W30 lubricant standard), FEPM copolymer of Fig. 1, and FKM Type 2 (improved lube resistance) of Fig. 2. The test data is reported in elastic shear modulus G' ($G=E/3$; $E=$ Young's modulus) rather than complex modulus E^* to better indicate elastic properties at a low strain amplitude (0.16%) and frequency (i.e. strain rate) (0.1 rad./sec) from -70°C to 150°C . This is within the so-called linear viscoelastic test region.

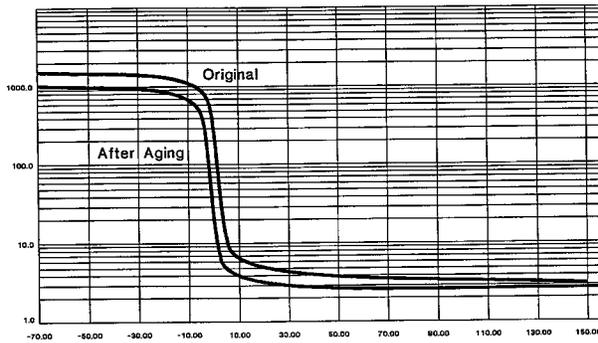


Figure 1: G' (MPa) vs. Temperature ($^{\circ}\text{C}$)

FEPM

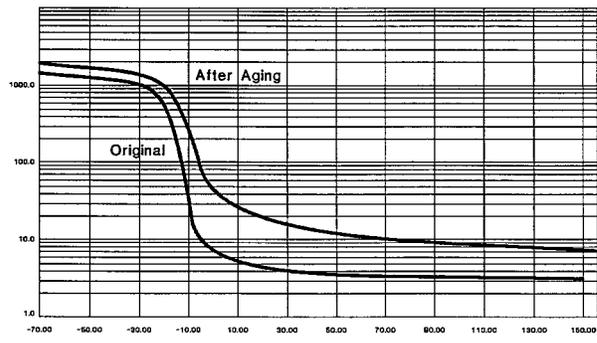


Figure 2: G' (MPa) vs. Temperature ($^{\circ}\text{C}$)

FKM Type 2

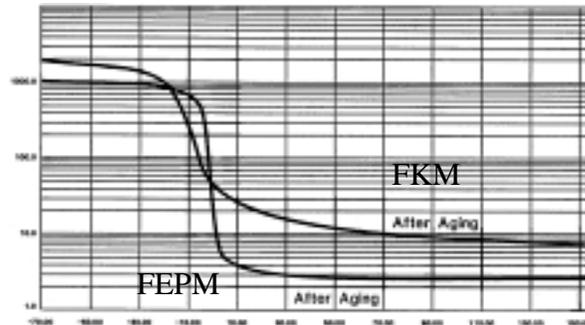


Figure 3: G' (MPa) vs. Temperature ($^{\circ}\text{C}$)

After Aging, FEPM & FKM Type 2

FKM Type 2 (Fig. 2) has a dynamic T_g of -20°C with an initial elastic shear modulus of 2.3 MPa at 100°C . After aging it increases to 7 MPa and the T_g increases to -15°C . FEPM copolymer (Fig. 1) has a dynamic T_g of 0°C with an initial elastic modulus of 3 MPa at 100°C . After aging it decreases to 2 MPa and the T_g decreases to -5°C . The DMRT clearly illustrates that the inhibitors in the lube oil have had a pronounced chemical effect of the FKM Type 2 elastomer. The FEPM copolymer is totally unaffected chemically and the

hydrocarbon component of SF105 has slightly plasticized the FEPM giving some improvement in low temperature superposing Fig (1) and Fig (2) onto Fig (3) clearly illustrates why FEPM might be the better candidate for a high-performance engine lube. DMRT data, although available, is not widely utilized and Farinella's (6) paper is an excellent reference.

Heat Resistance and Thermal Stability

In terms of heat resistance, all of the fluoroelastomers are capable of thousands of hours of service life at 200°C. One of the FFKM elastomers has been reported by its manufacturer to be capable of service as high as 300°C. Useful service life is often strongly influenced by design and application. In terms of physical properties, the strong ionic attraction between adjacent hydrogen and fluorine atoms contributes substantially to the room-temperature strength of fluoroelastomers. A typical fluoroelastomer loses 70% of its tensile strength at 100°C, while a hydrocarbon elastomer (EPDM) loses only 50%.

Thermal stability varies within the different fluoroelastomers. The vinylidene fluoride containing elastomers are slightly less stable due to thermally induced dehydrofluorination. These elastomers should not be used in a totally confined environment. Improvements in crosslink stability have been made over the past 15 years, but the thermal stability of all crosslinking systems appears to be lower than that of the corresponding elastomer.

References

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