

# FFKM to overcome new challenges

## An introduction to perfluoroelastomers

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*Perfluoroelastomers (FFKM) are polymer materials that come into play where other elastomers prove insufficient in handling chemical attacks and/or extreme temperatures. These materials have the highest level of chemical and thermal resistance of any elastomer currently available. They are more and more frequently successful in industry applications as operating conditions become increasingly intense and can be found in seals for engineering chemical installations, airplane turbines and plasma treatment related semiconductor applications. The intention of this article is to provide technical insight in FFKMs, their crosslink chemistry, chemical and thermal resistance, and application considerations. Also detailed information on how to handle and work with FFKM polymers/compounds will be provided. Due to their costs proper handling and use are significantly important.*

### 1. Introduction

Perfluoroelastomers are essential engineering materials that come into play where other elastomers prove insufficient in handling the harshest of chemical environments and/or extreme temperatures. These materials have the highest level of chemical and thermal resistance of any elastomer currently available. Perfluorinated elastomers (FFKM) are employed more often in many industry applications as operating conditions become increasingly intense.

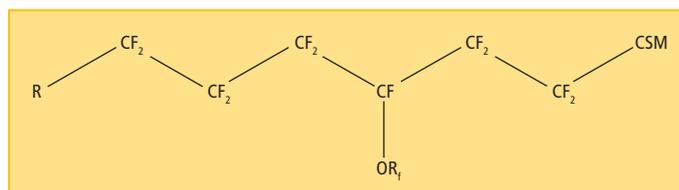
The intention of this article is to provide technical insight in FFKMs, their crosslink chemistry, chemical and thermal resistance, and application considerations. Also detailed information on how to handle and work with FFKM polymers/compounds will be provided. These materials are known to have much higher value than a typical

fluorocarbon (FKM) or hydrocarbon elastomer, so proper handling and use are important. However, a common misconception is that special equipment and/or environments are necessary to work with FFKMs. There are only minor handling and mixing considerations required. Typical FKM and hydrocarbon elastomer mixing and processing equipment is usually sufficient to work with FFKM materials.

### 2. What are FFKMs?

Perfluorinated elastomers, often referred to as FFKM(s) – as defined in the ASTM D1418 standard – are polymers that combine elastomeric behavior with the temperature and chemical inertness of PTFE. They are copolymers of (primarily) tetrafluoroethylene (TFE) and a perfluorinated vinyl ether (PFVE). In order to obtain elastomeric behavior while maintaining chemical inertness, they utilize a cure site monomer (CSM) to enable crosslinking. These cure site monomers typically contain a free-radically reactive bromine and/or iodine atom, or they carry a perfluoroalkyl nitrile group that can be induced to trimerize into a perfluorinated triazine network.

**Fig. 1:** Basic polymer architecture for a FFKM polymer made from tetrafluoroethylene and a perfluoro-vinylether (CSM -> cure site monomer)



Originally developed in the late 1960's, FFKM polymers contain approximately 72.5 % fluorine by weight and do not have any hydrocarbon segments in the polymer backbone.

Typical fluoroelastomers have a lower fluorine content, approximately 65.7 – 70.5 % by weight, and some available hydrocarbon character through the incorporation of various amounts of vinylidene fluoride monomer. Hydrocarbons can provide a thermodynamic weak point in standard fluoropolymers. The bond dissociation energy (BDE) of a fluorocarbon bond is approximately 20–30 % higher (depending on the reference used) than a hydrocarbon. The fluorocarbon BDE is 490 kJ/mol versus hydrocarbon bonds having a BDE of 410 kJ/mol.

The basic polymer architecture for a FFKM polymer made from tetrafluoroethylene and a perfluorovinylether is shown in **figure 1**. This structure is essentially the same for both the peroxide and high temperature (HT) catalyst grades. The CSM can be either an iodine- or a bromine-containing monomer (peroxide cure) or a nitrile containing monomer (catalyst cure). The R<sub>f</sub> group consists of a short chain fluorocarbon species, typically CF<sub>3</sub>.

### 3. FFKM crosslink chemistries

There are a few different crosslink chemistries used for FFKM polymers.

Early cure systems made use of diamines and later dihydroxy (bisphenolic) compounds to cure perfluorophenoxy containing backbones. Accelerators, like cyclic polyethers, were needed to achieve reasonable cure states.

Later, more common known systems were developed such as free-radical/co-agent cure and catalyst-induced triazine

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cure. Both methods will crosslink their respective FFKM polymers; however, they each have individual benefits and deficiencies. Care should be taken to choose the right cure chemistry and polymer combination for the end-use application being considered. 3M Dyneon Perfluoroelastomer Compounds are already incorporated with polymer/cure systems that give the optimum properties. Generally, a post-cure cycle is required in order to maximize the performance properties of either crosslink system.

### 3.1 Free radical cure system

The free-radical/coagent cure is mostly used for crosslinking standard FFKM grades. Using a reactive halogen containing cure site monomer (X-CSM; X=Br or I) and a suitable coagent to trap the peroxide generated free radicals, this type of crosslink is excellent for application temperatures up to about 230 °C, and can be used in steam, acid, and hot water applications. However, such compounds do not have as good thermal (compression set) performance as the triazine type cured materials.

To crosslink the standard grade FFKM polymers, triallyl isocyanurate (TAIC) has been shown to give the best overall performance as a coagent with regard to physical properties and heat resistance. TAIC can migrate away from the polymer and homopolymerize readily during the cure cycle. As such, it can affect processability, e. g. mold fouling, and

sometimes trimethylallyl isocyanurate (TMAIC) is used instead. Some improvements to compression set have been obtained by using or blending TAIC with TMAIC, which will slightly retard the cure rate allowing for a more ordered crosslink network to develop during cure. **Figure 2** shows the chemical structure of TAIC and TMAIC.

Because these reactions are peroxide initiated, these materials can become scorchy. Good temperature control and care during mixing and processing the chemical FFKM polymers/compounds is therefore vital. Typically, dialkyl peroxides such as 2,5-dimethyl-2,5-di(t-butylperoxy)hexane (DBPH, **fig. 3**) are used to help impede scorching. Different peroxide initiators can be used to fine tune the cure rate.

### 3.2 Triazine cure system

To form the triazine crosslink network in the HT FFKM grades, a proprietary catalyst is employed, reacting at a high temperature with nitrile containing cure sites (CN-CSM), polymerized in the backbone, to form a triazine ring structure shown in **figure 4**.

This aromatic heterocyclic structure is very thermally stable and has shown good performance for continuous use up to 316 °C. Overall chemical resistance is very good. The CN-CSM can be incorporated into the polymer at various concentrations in order to obtain different crosslink densities. The Achilles heel of this crosslink chemistry is its suscep-

tibility to hydrolysis by amines, steam and/or hot water. Upon exposure, the ring will open through aromatic nucleophilic substitution affecting sealing and physical performance.

### 3.3 Other nitrile cure systems

Another way to cure nitrile containing perfluoroelastomers is by applying the benzoxazole crosslinking. Bisaminophenol is used as cure agent. Good thermal stability can be achieved to approximately 275–280 °C.

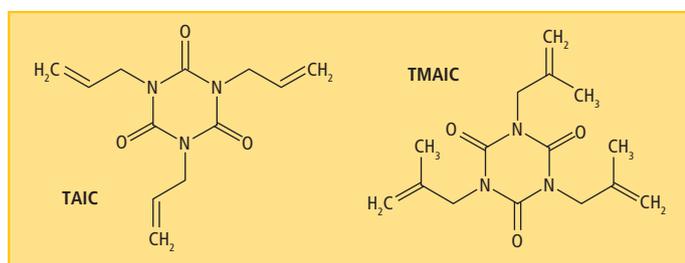
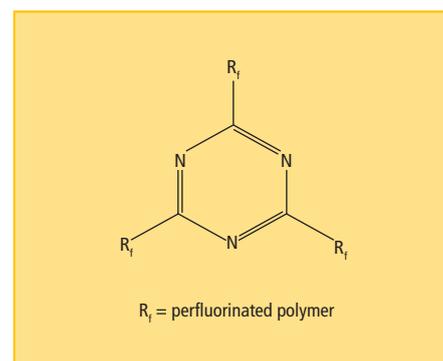
Nitrile containing FFKMs can also be used by using a radical PO/coagent cure system. Chemical resistance is greatly improved compared to the triazine crosslink but at a compromise of the temperature resistance.

## 4. Processing of FFKMs

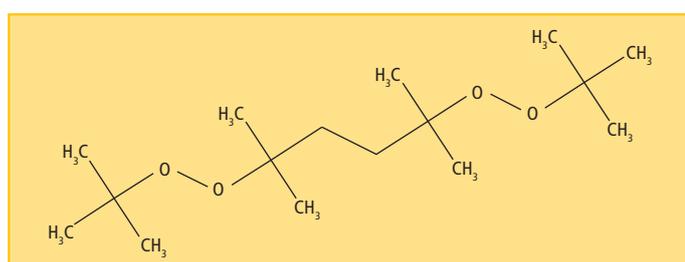
### 4.1 Compounding and mixing

Select the cure chemistry appropriate for the grade of FFKM being utilized and/or application conditions when formulating FFKM compounds. Neat curatives and additives should be used whenever possible to achieve the best performance. This is especially true for steam and acid exposure applications. Keep in mind that non-fluorinated additives will have a tendency to migrate out of the perfluoroelastomer due to their inherent oleophobic and hydrophobic nature. This migration may be so fast as to occur already during the mixing process. Any processing step involving shear conditions further contributes to this phase separation behavior.

**Fig. 4:** Triazine ring structure of a triazine crosslink network



**Fig. 2:** Chemical structure of TAIC and TMAIC



**Fig. 3:** Chemical structure of 2,5-dimethyl-2,5-di(t-butylperoxy)hexane (DBPH)

Other components should be used as needed. For fillers, both carbon black and mineral fillers can be used. Typical carbon blacks used are MT, FEF, SRF, and HAF types, e. g. MT N990, FEF N550, SRF N770, and HAF N330. Common mineral fillers can be employed as well, e. g. barium sulfate, Min-U-Sil 5.

Specific process aids can be used with FFKMs and only as needed. Peroxide FFKM grades benefit from the addition of zinc oxide, acting as an acid acceptor and improving compression set performance. Note, however, that resistance to certain chemicals, e. g. acids, is further affected by the compound ingredients. For example, if acid acceptors, such as zinc oxide, are used, the acid resistance of the finished part is negatively affected.

A typical start formulation for PFE 90Z is given by **table 1**. This formulation would result in good heat resistance although the amount of ZnO should be lowered to get the best acid resistance.

Perfluoroelastomers can be mixed using standard elastomer mixing equipment. For best results, mill mixing is recommended. As with any fluoroelastomer mix, the mill or internal mixer should be very clean and free of contaminants, especially moisture – HT FFKM grades are moisture sensitive. Also, small amounts of standard FKMs, even as much as 500 ppm, can have an effect on cure rate. It is recommended that all other raw ingredients are pre-blended to better facilitate incorporation into and dispersion throughout the polymer.

When starting the mix, the mill gap should be wider than usual, mainly due to the higher stiffness caused by the high F content and the high molecular weight. After passing the FFKM polymer through once or twice, slowly close the nip until a normal mix gap is reached. Key to mixing FFKM is to keep the compound warm to the touch. Add the pre-blended ingredients in several additions. Adding too quickly can cause the polymer band to break and crumble apart. If this happens, the material can be patiently worked back together, but should be avoided by incremental additions. Stay at, or below, the recommended safe temperature for peroxide mixing.

**4.2 Storage**

FFKM compounds are preferably stored in the fridge in an air sealed bag. Alternative is in a climate controlled area. Always keep it away from moisture. Allow conditioning to room temperature in the bag prior to opening/use in order to avoid condensation on the compound.

**4.3 Remilling and preheating**

Though usually not needed it can be useful that the compounds are refreshed and/or warmed (~60–70 °C) for 5–15 min prior to use. This will help with flow, reincorporation of any additive(s) that may have begun to migrate out of the mixed FFKM polymer, and further improve filler dispersion. As with the mixing above, make sure to start with a wide nip and slowly close as the material warms. Cold FFKM compounds and a narrow mill gap can damage equipment.

**4.4 Compression molding**

Compression molding is recommended for manufacturing FFKM articles. Pre-forms should be as close as possible to the size of the finished part to decrease the distance the material has to flow in the mold as well as potentially limit expensive flash. Recommended molds are made of stainless steel – but not all stainless steel is ok. Particularly recommended is to use Stavax ESR stainless steel. Typically two degassing cycles, to release any trapped gases, are sufficient but up to 3–4 bumpings can be done – depending on the finished part. Mold release might eventually be used for peroxide cured compounds for reasons mentioned in the crosslink chemistry section above. Stoner A373 fluoroelastomer release agent has been found to work very well for FFKM compound molding – please make sure to closely follow the supplier’s application instructions. Mold release agents are typically not necessary to use with our provided compound systems.

**4.5 Extrusion**

Perfluoroelastomers can also be extruded easily, which is the regular practice to make preform cord. Zone (barrel) temperatures of

about 50–80 °C and nozzle temperatures of 70–90 °C give good results.

**4.6 Injection molding**

Though commercially seldom used 3M’s FFKM compounds have very good injection molding capability. Triazine cured compounds need a longer cycle time of about 10 min, but mold release is extraordinarily good. An extra advantage to obtain good flow of the latter compounds is that barrel temperatures can be as high as 120 °C without compromising scorch safety, thereby greatly improving the mold flow.

**4.7 Vulcanization**

Cure conditions will vary with the crosslink system used. For a peroxide cure, 10 min at 177 °C is a recommended starting cure cycle. The catalyst-induced triazine cures require a slightly longer cycle time and somewhat higher cure temperature. Typical cure times are 15 min at 187 °C in order to attain sufficient strength out of the mold. For thicker parts, it is recommended to lower cure temperatures to as low as 160 °C and lengthen the cure cycle.

As with the press cure conditions above, the post-cure conditions are curative dependent as well. Recommended starting settings for peroxide initiated systems are 4–16 hours at 200–230 °C. Actual time will depend on final performance requirements. The HT FFKM grades typically are post-cured in air for 24 hours at 250 °C. Sometimes a post-cure under nitrogen atmosphere up to 310 °C is applied in order to achieve ultimate high temperature compression set resistance. For thick parts, a step post-cure might be necessary. Please note that a typical FFKM compound will have a shrinkage of ~3.5 % after post-cure. The actual value will be formulation and processing dependent.

**Tab. 1:** Typical start formulation for FFKM PFE 90Z

Ingredient	Amount / phr
PFE 90Z	100
Carbon black MT N990	20
ZnO	5
Trigonox 101-50D	1.5
Luvomaxx TAIC-70 DL	2.5

**Table 2** shows the recommended press and post-cure temperatures for 3M's product range.

#### 4.8 Metal bonding of FFKM compounds

When bonding FFKM materials, only use un-crosslinked compound. It is extraordinarily difficult to bond to cured perfluoro-elastomers. The use of process aids should be minimized or completely eliminated if possible when attempting to bond FFKM. While no special adhesives currently exist for perfluorinated materials, experience has shown that good bondability can be achieved using Lord Corporation's Chemlok 5150 and Dow Chemical Corporation's Megum 3290-1.

As with any adhesive application process, closely follow the supplier's instructions for surface preparation and adhesive application. Mostly a pre-bake of the adhesive layer at a low temperature (150 – 160 °C) for ~5 min can be useful in adhesion promotion to metal substrates prior to molding. After molding the bonded article, a post-cure will likely be necessary. Because the adhesives cannot handle extreme temperatures for long periods of time, it is recommended that a shorter post-cure time will be used at typical post-cure temperatures (~230 °C) or post-cure for a longer time using a lower temperature (200 °C) when bonding FFKM.

### 5. FFKM markets and applications

Historically, FFKM has been used primarily in very specific and/or highly technical applications, such as aerospace and the semiconductor industry. More recently, the material is gaining a wider acceptance and necessity in the transportation (not just aerospace), chemical processing industry (CPI), and oil and gas markets due to increasingly demanding application environ-

ments. The high cost of these materials may be a barrier for many applications. FFKM is now more commonly used in many markets where FKM was almost 35 years ago. While expensive compared to other materials, it is often chosen when other material choices have failed. The costs associated with the utilization of FFKM in desired applications are in line with the expected benefits gained from the efficacy of the final material solution.

Much of the initial use for FFKM was in aerospace for use with some of the very corrosive lubricants and fuel additives for airliners, not to mention the high temperature exposure for many seals and other elastomeric components. In the semiconductor market, the need for plasma, chemical and thermal resistance made FFKM an absolute requirement in semiconductor processing and use in finished electronic devices. As automobile and heavy equipment engines and their respective components continue to see more aggressive fluids and higher operating temperatures, the use of FFKM is expected to increase in automotive, heavy duty, and marine.

The price of oil is projected to rise, as the oil and gas industry has to work harder and spend more to get the precious commodity out of the earth. The days of simply drilling into the ground and having oil come out are gone. Deeper wells are being drilled, at higher and higher temperatures in more chemically aggressive environments. The need for materials that will not fail under extreme conditions is more critical than before. FFKM fills that gap for many applications.

There are a variety of applications for FFKM in the CPI market as well. From taking oil and refining it into other useful chemicals, to fluid transport, and machinery-/material handling equipment, FFKM is finding a new home in many areas where improved chemical resistance is necessary. Applications

include stators/progressive cavity pumps for moving chemicals, line stops for use in maintenance at CPI plants, and seals for valves and pumps having exposure to harsh materials, extending their useful life and providing increased reliability and safety.

### 6. Application considerations for FFKM

When considering an FFKM material for use in an application there are several considerations to be made to make sure the right FFKM polymer and/or compound is chosen. Also engineering considerations have to be made. Following issues should be clarified beforehand:

- What is the application temperature? Are there possible excursions to higher temperatures? Up to what temperature and for how long?
  - a: For temperatures up to <230 °C, basically all FFKM grades can be used.
  - b: For temperatures up to >230 °C, all except the standard PO based product
- What chemicals will the finished article be exposed to?
- What are the physical property requirements?
  - a: Tensile, elongation, modulus, hardness, tear resistance
  - b: Compression set
- Which compression will the FFKM seals be exposed to in application - related to high CTE (coefficient of thermal expansion), see below?
  - a: Recommend <20 % deflection for temperatures >300 °C (e. g. 18 %).
  - b: Recommend <30 % deflection for all other temperatures (e. g. 25 %)
- Will the article go into a static or dynamic application?
- Does the FFKM need to be adhered to a substrate?
- How will the article be manufactured?

### 7. FFKM coefficient of thermal expansion

An important consideration for FFKM materials is their high coefficient of thermal expansion (CTE) compared to other mate-

**Tab. 2:** Recommended press- and post-cure temperatures for 3M's product range

Product	PFE 90Z compound	PFE 7502 BZ	PFE 7301 BZ	E-21464	PFE 7403 WZ
Press-cure	10 min / 177 °C	15 min / 177 °C	15 min / 187 °C	15 min / 177 °C	15 min / 187 °C
Post-cure	16 h / 230 °C	24 h / 250 °C	24 h / 250 °C	Ramp up 200 to 310 °C in 8 hours	24 h / 250 °C

rials, including standard FKM. In this light, special care should be taken in the groove design to avoid overload and gap extrusion. For a relative idea of the difference in CTE, a FFKM was evaluated against an FKM. The samples tested were peroxide cured formulations containing the same amount and type of filler (N990 Carbon Black).

Samples were run on a TA Instruments Q400 thermomechanical analyzer (TMA) heating and cooling between -50 °C and 225 °C at a rate of 5 °C/min using a macro-expansion probe for testing. A summary of the CTE values determined from analyzing the TMA data is tabulated in **table 3**.

The FFKM sample has an average CTE increase of ~30 % compared to the FKM with the same filler loading. The actual CTE of any finished compound will be formulation dependent. Increasing the filler content will result in a decrease of the CTE, as fillers are having a significantly lower CTE value (e. g. carbon black = 0.20 µm/m·°C).

### 8. Available FFKM grades

3M offers different types of FFKM. 3M Dyneon Perfluoroelastomer PFE 90Z, provided as a gum, can be crosslinked using a suitable peroxide and a coagent. This grade is meant for applications where chemical resistance is the primary concern and temperatures will not be higher than 230 °C. This grade tends to be more economical compared to other FFKM grades and is good for chemical handling and processing, cleaning, and chemical etching processes in a variety of industries.

3M Dyneon Perfluoroelastomer PFE 7301BZ and E-21464 HeatShield, provided as compounds, are the so-called high temperature (HT) grades using proprietary catalyst chemistry to form a triazine crosslink network and are used when temperatures are in excess of 230 °C. These perfluorinated triazine networks are capable of performing at temperatures continuously up to 316 °C with minimal loss of properties and outstanding compression set resistance. Outstanding sealing ability for prolonged exposure to the highest possible temperatures and aggressive aerospace fluid environments are the key re-

quirements for FFKM materials supplied to the aviation industry for engine sealing applications. 3M Dyneon Perfluoroelastomer PFE 7301BZ HeatShield has, for many years, proven to meet the demands of the aerospace market for high temperature sealing solutions. More recently, the development of E-21464 HeatShield demonstrates even further enhancement of the already outstanding long-term, high temperature (316 °C) compression set resistance of PFE 7301BZ. It takes the performance of high temperature FFKM materials to an even higher level and ready to serve future generations of high temperature jet engine applications. The HT FFKM grades are, next to their usage in the aerospace industry, excellent for many thermally extreme processes with exposure to aggressive chemicals in oil and gas, and chemical process industry applications. The only drawback is the lower performance of these products in hot water, steam and ethylenediamine applications.

3M also introduced a novel third system which has overcome the technical challenges faced in combining both of these features into one single technology, for one single

product. The new development 3M Dyneon Perfluoroelastomer PFE 7502BZ ChemShield is a proprietary, black, 75 Shore A compound with excellent chemical resistance and continuous operating temperature at 275 °C. This compound is also compliant with the USP VI and FDA requirements, making it a universal product.

The semiconductor industry requires, next to the inherent chemical and thermal resistance, high purity products. The smallest particulate or gaseous contaminant in the production process can lead to quality issues for the final product. Materials and process purity as well as cleanliness are of paramount importance. 3M Dyneon Perfluoroelastomer PFE 7403WZ PlasmaShield is suitable for the most challenging semiconductor manufacturing processes, where regular contact with oxygenated and fluorinated plasma treatments is a prerequisite. During such plasma treatments, the weight loss, emissions of particles, and outgassing of PFE 7403WZ is minimal (**fig. 5**). To get the maximum benefits of these materials, they should be handled and converted to finished articles in a clean room environment.

**Tab. 3:** CTE and T<sub>g</sub> values of FKM and FFKM from TMA analysis

Sample ID	Durometer in Shore A	Heat up CTE in µm/m·°C	Cool down CTE in µm/m·°C	Heat up T <sub>g</sub> in °C	Cool down T <sub>g</sub> in °C
FKM 30 phr N990	69	260.5	295.1	-24.35	-25.54
FFKM 30 phr N990	75	340.3	384.2	-1.61	-2.95

**Tab. 4:** Typical mechanical properties of 3M's currently available perfluoroelastomer compounds

Properties	HeatShield PFE 7301BZ	HeatShield E-21464 (innovation)	ChemShield PFE 7502BZ	PlasmaShield PFE 7403WZ	PFE 90Z Gum
Maximum continuous temperature in °C	316	316	275	316	230
<b>Compression set</b>					
70 h at 200 °C in %	14	14	15	18	29
70 h at maximum continuous temperature in % / °C	44 / 316	29 / 316	40 / 275	58 / 316	37* / 230
<b>Physical properties</b>					
Tensile strength in MPa	17.0	10.3	15.8	10.6	19.8*
M100 in MPa	12.5	8.8	11.6	4.7	13.1*
Elongation at break in %	153	149	129	230	134*
Hardness in Shore A	80	80	76	74	73*
Color	Black	Black	Black	White	Opaque, off-white
<b>Chemical resistance</b>	High temperature stability, hydraulic oils	Best compression set and long-term performance at highest temperatures	Solvents, acids, bases, amines, water and steam - USP VI	Fluorinated and oxygenated plasmas	Broad chemical resistance against acids, bases, solvents, fuels and oils
* With typical compound formulation					

## 9. Typical properties of FFKM

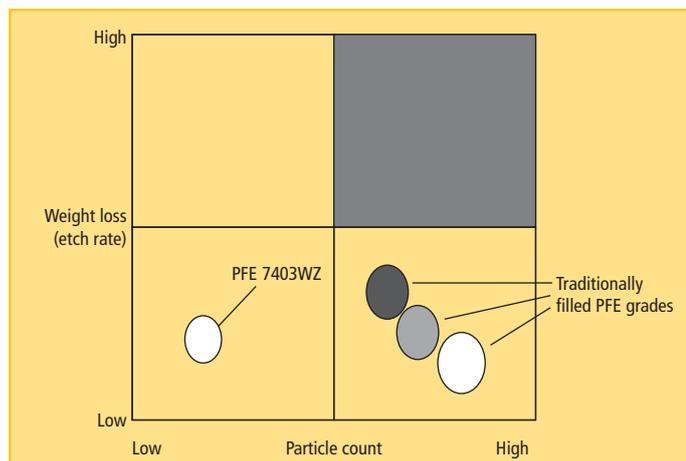
**Table 4** presents the properties of 3M's available compounds. Please note that for compression sets up to 230 °C, a 25 % deflection is used, and for >300 °C, only 18 % deflection was imposed on the test specimens due to the much higher coefficient of thermal expansion of FFKM polymers as compared to FKM or hydrocarbon elastomers.

Aggressive environments require individual material solutions. 3M has developed a range of custom FFKM products that face up to the specific challenges of temperature and harsh chemicals as encountered in the aerospace, chemical processing and the semiconductor industries.

**Tab. 5:** Chemical resistance of PFE 7502BZ ChemShield compared with a typical FKM

Chemical resistance (hot fluids)	FKM	PFE 7502BZ ChemShield
<b>Acids</b>	→+	++
– hydrochloric	→+	++
– nitric	–	++
– sulfuric	→+	++
– acetic (glacial)	–	++
<b>Solvents</b>	–	++
<b>Bases (NH<sub>4</sub>OH, NaOH)</b>	–	++
<b>Ethylenediamine</b>	–	+
<b>Water</b>	→+	++
<b>Steam</b>	→+	++
<b>Continuous temperature in °C</b>	220	275
<b>Compression set 70 h, 25 %, 200 °C in %</b>	15	15

**Fig. 5:** Comparison of relative weight loss and particle emission of different perfluoroelastomers during plasma treatment



## 10. Resistance of FFKM

### 10.1 Chemical resistance

For all FFKM polymers and cure types, resistance to a wide variety of chemicals, at varying concentrations and conditions, is exceptional. Chemistries, such as polar solvents, that would normally affect other fluoroelastomers negatively have little to no effect upon the fully fluorinated elastomers.

**Table 5** shows a comparison in chemical resistance of PFE 7502BZ ChemShield and a typical FKM. FFKM gives superior performance against every chemical involved in the process.

In **figure 6** the excellent all-round chemical resistance of 3M Dyneon Fluoroelastomer PFE 7502BZ ChemShield is demonstrated. The low volume swell results provide evidence of the outstanding chemical resistance to water, steam, primary and tertiary amines, acids, bases and solvents. This makes PFE 7502BZ the ideal candidate for meeting the requirements of the chemical processing industry.

### 10.2 Thermal resistance

Thermal resistance of FFKM materials is exceptional as well, even with exposure to harmful chemistries. For the peroxide/co-agent FFKM grades, application use to approximately 230 °C is feasible. The upper temperature range is significantly increased for the HT grades to 316 °C because of the

exceptional thermal stability of the triazine crosslink.

The compression set resistance is an indication of the ability of the polymer to retain its "elastic memory". Temperature is one of the most important causes of compression set increase over time and sealing failure. With increasing temperature the bonds that make up the polymer backbone and the crosslinks can be broken. In **figure 7** one can see the outstanding compression set retention of the triazine cured PFE 7301BZ. Note that the regular peroxide cured product cannot be used at high temperatures.

Further work on thermal resistance was done using the Arrhenius model. The Arrhenius model can be used when the rate of a chemical reaction (or property change) is proportional in time. The reaction/degradation rate and temperature relationship is represented by the Arrhenius equation:

$$\ln(k) = -E_a/RT + \ln(A) \quad 1$$

where

$k$  → rate of decomposition (e. g. % wt loss x min<sup>-1</sup>)

$E_a$  → activation energy (J x mol<sup>-1</sup>)

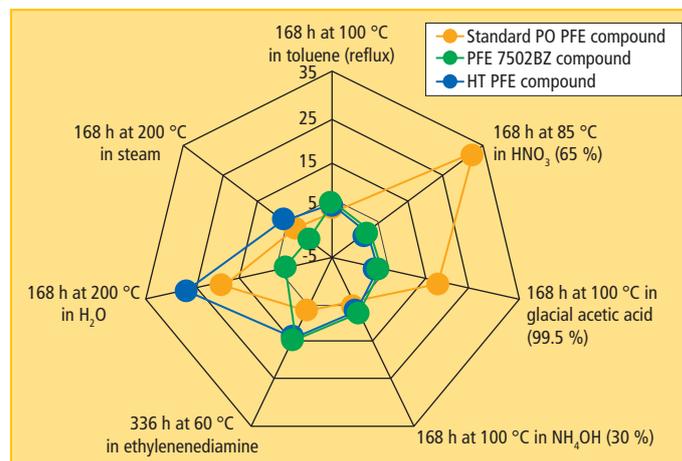
$R$  → universal gas constant (8.31451 J x mol<sup>-1</sup> x K<sup>-1</sup>)

$T$  → temperature (K)

$A$  → frequency factor

One method to predict usefulness of elastomers at a certain temperature is by con-

**Fig. 6:** Comparing % volume swell data of PFE 7502BZ compound, a standard PO PFE compound and HT PFE compound



ducting isothermal thermogravimetric analysis (isothermal TGA). This method uses TGA measurements in air at various temperatures till a certain weight loss (e. g. 5 %).

Figure 8 shows an example of the measurements for PFE 7301BZ. At various temperatures the time was measured till the compound lost 5 % weight.

Using the slope  $(-30.2 \times 10^3)$  of the Arrhenius plot  $(y = ax + b \rightarrow y = -30.2x + 43.224)$ , the activation energy  $E_a$   $(-\text{slope} \times R)$  for thermal decomposition of the sample is 251 kJ/mol.

Also temperatures at which 1, 5 and 10 % weight loss is expected after 1,000 hours can be calculated by equation 2

$$T = -E_a/R \times (\ln(k) - \ln(A)) \quad 2$$

giving the following results for PFE 7301BZ:

- 1 % weight loss after 1,000 h: 284 °C
- 5 % weight loss after 1,000 h: 301 °C
- 10 % weight loss after 1,000 h: 309 °C

Table 6 summarizes the results for 3M's perfluoroelastomer product line. Note that these values only take into account weight loss by thermo-oxidative degradation and do not take into account the quality of the cured network.

In order to include this very important factor, long-term compression sets were run to estimate the real upper use tempera-

ture or lifetime prediction. The assumption was made that lifetime temperature would be reached when compression set is 80 % after one month of continuous exposure to that temperature. Long-term compression set data was obtained to calculate the time when 80 % compression set was reached. This can be seen in figure 9 for PFE 7301BZ as example.

The time to reach 80 % compression set can be calculated according to equation 3:

$$x = e^{(y + b)/a} \quad 3$$

The results are given in table 7. They refer to the example illustrated in figure 9. Note that PFE 7301BZ will last for 138 years (!) in a static environment when exposed

to a continuous temperature of 225 °C and 1.3 years at a temperature of 275 °C. This data could support even the use of this kind of expensive material at lower temperatures, when downtime is to be avoided at all.

When acquiring the data at different temperatures Arrhenius can be applied again to predict the lifetime temperature (= temperature at which compression set reaches 80 % under continuous exposure to that specific temperature). Table 8 shows the corresponding data for PFE 7301BZ.

Figure 10 demonstrates the graphical evaluation of data from table 8.

When solving the Arrhenius equation (eq. 2) for T and using the data derived from

Tab. 6: Comparing the thermal resistance of 3M's FFKM grades. The rating is based on the activation energy for thermal degradation and the weight loss after 1,000 h as a function of temperature exposure.

FFKM grade	Activation energy $E_a$ in kJ/mol	Temperature needed for 1,000 h weight loss in °C		
		1 % Weight loss	5 % Weight loss	10 % Weight loss
PFE 90Z compound	190	241	261	269
PFE 7502BZ	228	270	288	296
PFE 7301BZ	251	284	301	309
E-21464	261	290	307	314
PFE 7403WZ	228	272	290	298

Tab. 7: Service life data of PFE 7301BZ – calculated from results in figure 9

PFE 7301BZ at service temperature in °C	Slope a	Intercept b	Time till 80 % compression set			
			Hours	Days	Years	R <sup>2</sup>
225	6.282	-7.99	1,210,796	50,450	138	0.9956
275	9.8616	-11.92	11,166	465	1.3	0.9907

Fig. 7: Comparative long-term compression set at 225 °C and 275 °C for different FFKM grades

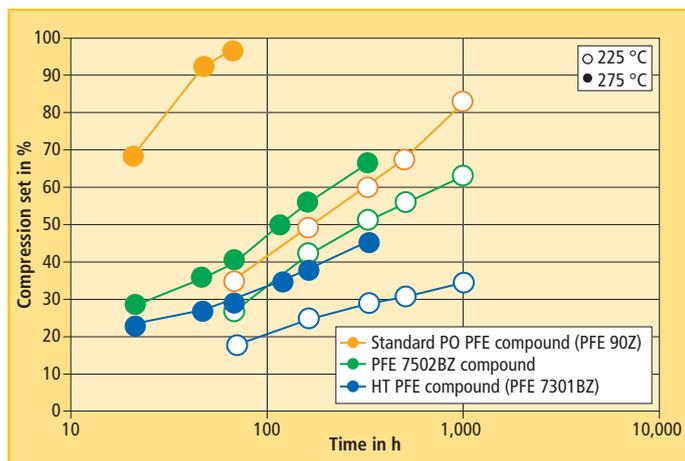
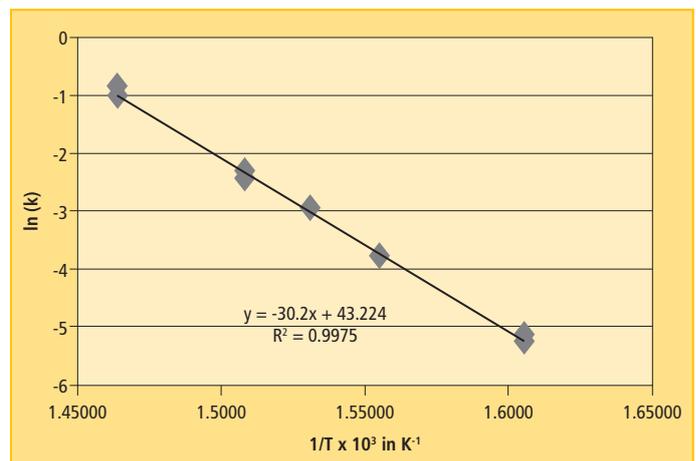


Fig. 8: Isothermal TGA measurements for PFE 7301BZ – different temperatures for 5 % weight loss



**figure 10** (slope  $a = -22.762 = E_a/R$  and intercept  $b = 36.467 = \ln(A)$ ), then results for PFE 7301BZ a maximum service temperature of 316 °C at which compression set reaches 80 % after one month. Similar data for other FFKM grades gave the following estimated maximum lifetime temperature (one month lifetime, 80 % compression set): for PFE 7502BZ a temperature of 277 °C

and for PFE 90Z compound a temperature of 229 °C respectively.

## 11. Conclusions and outlook

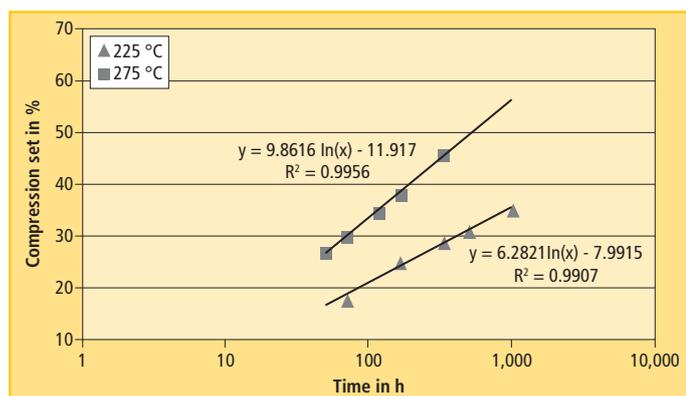
Perfluoroelastomers are used for the most extreme of chemical and thermal conditions in a wide range of industries. Where other

materials fail, FFKM can perform successfully. Specialized equipment is superfluous for processing FFKM polymers. Some training and know-how is all that is required. Actual performance is dictated by many factors, including but not limited to compound formulation, crosslink chemistry and density, polymer molecular weight, manufacturing conditions and application conditions. All factors should be weighed thoroughly prior to choosing a FFKM grade. The methods for estimating lifetime and maximum service temperature for a given service time described in this article prove to give more realistic data than was obtained by thermogravimetric analysis data. More evaluations on 3M's complete FFKM product portfolio are underway.

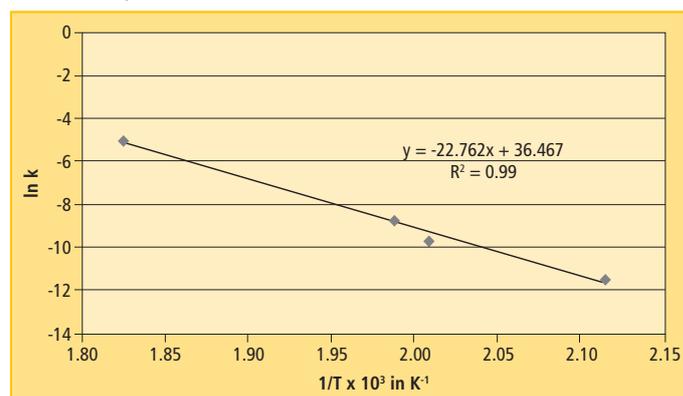
**Tab. 8:** Service life data and Arrhenius calculation for PFE 7301BZ as a function of temperature

PFE 7301BZ at service temperature in °C	Time in h	Temperature in K	1/T in K <sup>-1</sup>	k in h	ln(k)
200	7,309,479	473.15	0.002113	0.0000109	-11.422656
225	1,210,796	498.15	0.002007	0.0000661	-9.624762
230	483,973	503.15	0.001987	0.0001653	-8.707758
275	11,166	548.15	0.001824	0.0071646	-4.938602

**Fig. 9:** Long-term compression set of PFE 7301BZ at different temperatures



**Fig. 10:** Graphical evaluation of table 8 – service life of PFE 7301BZ at different temperatures



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