

New Low Temperature Fluoroelastomers with Novel Monomer Compositions Characterized for Oilfield Service

[Steven Jagels](#), Peter Farrow, Fabiano Merli, Giovanni Comino

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Abstract: With exploration and service environments becoming more extreme in both hot and cold temperatures, fluid resistant elastomers with a wider temperature performance window are needed. A new fluorinated monomer technology is now extending the dynamic low temperature capability of fluoroelastomers (FKM) to -40°C while improving fluid resistance compared to the older generation of low temperature fluoroelastomers. The paper describes and characterizes these new low temperature polymers for applications in the oilfield.

INTRODUCTION

Fluoroelastomers (FKM) are utilized extensively in severe environments within the oil and gas industry. The development of a range of fluorinated monomers has allowed different types of FKM to be commercialized to meet specific performance requirements. The selection of FKM for a particular oil and gas application can involve balancing thermal and chemical resistance with the ability to seal at low temperature. Other considerations for sealing materials are extrusion resistance and the capability to survive rapid gas decompression (RGD) events. Engineers are searching for sealing materials which can satisfy these ever increasing technical demands.

FKM types are classified according to their monomer constituents by ASTM D1418-05ⁱ. This classification allows general assumptions to be made regarding the performance of each type. However, the exact monomer composition and sequencing during polymerization combined with the cure system have a significant impact on the final performance of the material which is not accounted for in the specification.

The key monomer that has historically been used for extending the low temperature performance of FKM has been perfluoromethylvinylether (PMVE). The replacement of hexafluoropropylene (HFP) by PMVE enabled FKM materials to be developed with glass transition temperatures in the region of -30°C . Novel monomer types have recently been developed to lower the glass transition temperature to -40°C and simultaneously improve the chemical resistance profile of the next generation of low temperature FKM materials. This technology is now available to the oil and gas industry as high pressure, low temperature (HPLT) sealing capability becomes an important design consideration.

Use of Low Temperature Fluoroelastomers in Oil and Gas Applications

Advances in polymerization technology have improved peroxide curable fluoroelastomers (FKM) to a stage where they are the preferred FKM polymer for oil and gas applications. It is well known that bisphenolic cured FKM materials are more sensitive to mixed fluid environments containing amines and water while peroxide curable FKM materials are more resistant to amines, sour gas and water based fluids. The peroxide cure system in FKM does not create unsaturations in the polymer backbone as does bisphenolic (ionic) curing. Peroxide curing results in fewer sites for aggressive fluids to attack leading to long-term environmental resistance and stability.

Existing low temperature, peroxide curable FKM based compounds have been reported to work at temperatures and pressures up to 200°C and 25,000 psi and in the presence of complex chemical mixtures including H₂S and CO₂. The development of these compounds has resulted in superior performance compared to bisphenolic cured FKM compounds, particularly in high pressure, high temperature (HPHT) applications.

Whilst the trend towards HPHT environments has been well documented within the industry, another sealing requirement is now warranting further consideration – high pressure, low temperature (HPLT) as well as standard low temperature sealing capabilityⁱⁱ. As exploration and production (E&P) activity spreads to extreme climates such as the Arctic Circle, seals must be able to perform in both surface and downhole conditions at increasingly lower temperature environments.

Surface sealing applications such as within compressors, valves and pumps demand HPLT performance down to temperatures as low as -40°C. For downhole applications, drilling and completion tools are often tested on the surface before being used in the well and if the surface temperature is low enough, a standard FKM seal may fail the specified test. Cold tools on the surface may be thermally shocked as they are lowered downhole and elastomeric seals must remain flexible during the thermal shock of hot fluid and a cold tool to maintain a seal. Subsea tools and equipment may be utilized when ocean temperatures are close to 0°C which is below the glass transition temperature (T_g) of certain fluorinated elastomers leading to potential seal failure.

New technology has enabled the commercialization of low temperature FKM with glass transition temperatures as low as -41°C. This has been achieved without compromising other desirable properties such as long term sealing force, compression set, fluid resistance and thermal ageing performance. The objective has been to satisfy both surface and downhole applications in HPHT and HPLT environments and provide further options for equipment design.

Low Temperature Fluoroelastomer Technology

The T_g of typical fluoroelastomer copolymers (VDF/HFP) and terpolymers (VDF/HFP/TFE) is in the range of -25 to -10°C. When HFP is substituted by PMVE, the T_g can be lowered in the range of -30°C. Given that PMVE substitution will only drop the T_g to near -30°C; new monomers are needed to significantly improve the low temperature performance of an FKM.

The presence of more than one ether oxygen in the pendant group of the perfluoro-vinylether substantially reduces the T_g. However, the amount of oxygen in the pendant group is not sufficient to characterize the ability of the perfluoro-vinylether to lower the T_g of fluoroelastomers. In particular, specific vinylethers such as perfluoro methoxyvinylethers, named MOVE hereafter, having general formula of the type CF₂=CF-OCF₂O-R_f, are particularly effective. Experimental work has shown that the T_g of fluoroelastomers that incorporate MOVE monomer are well below the values expectedⁱⁱⁱ from applying known model equations (Gordon-Taylor^{iv} equations or Fox^v), making it necessary to explain the experimental data by the introduction of models that account for the effect of monomer sequences^{vi,vii} (see figure 1).

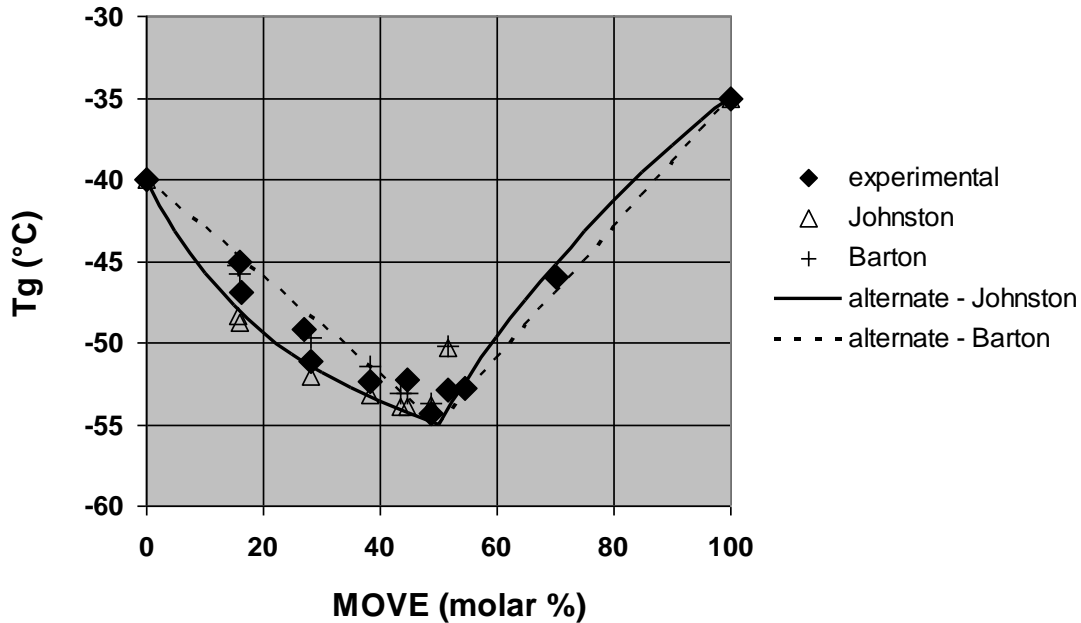


Figure 1: Glass transitions of VDF/ MOVE copolymers: comparison of the experimental values with those calculated using Johnston and Barton equations from measured dyad contents. The continuous and dotted lines refer to the ideal cases of purely alternated polymers.

It is discovered that MOVE's performance in lowering the glass transition of a polymer is magnified when polymerization utilizes branching and pseudo-living polymerization (B&PL). B&PL enables the design of complex 3-D networked FKM polymers with excellent physical properties. The dual combination of MOVE, B&PL technologies, with optimized polymerization variables (i.e. pressure and temperature) opens the door to a new generation of LT FKMs having new monomer composition and sequences. These new polymers along with optimized molecular weight and molecular weight distribution can create the performance profile required for elastomers in HPLT oil and gas applications.

The development an efficient process for the production of MOVE monomer which was found to be the best perfluorinated monomer for the production of very low glass transition temperature fluoroelastomers^{viii,ix,x}. This efficient process technology has allowed the commercialization and scale up for large production volumes of polymers with MOVE constituents.

The first polymer developments with MOVE have been peroxide curable fluoroelastomer grades with glass transition temperatures in the range -40°C and designed for both compression molding and injection molding. The compositions have been optimized to combine the chemical resistance typical of peroxide curable fluoroelastomers and excellent mechanical properties with a very low glass transition. The main feature of the technology is the optimization of low temperature performance while maintaining outstanding sealing properties. In particular, the temperature retraction test (Tr Test) shows very low Tr10 value almost coinciding with the T_g value (see figure 2). Moreover, the Tr curve is very sharp, giving all typical values grouped in a narrow range, $\Delta(T_{r70}-T_{r10}) \sim 6^\circ\text{C}$, indicating a good compositional homogeneity (see figure 2).

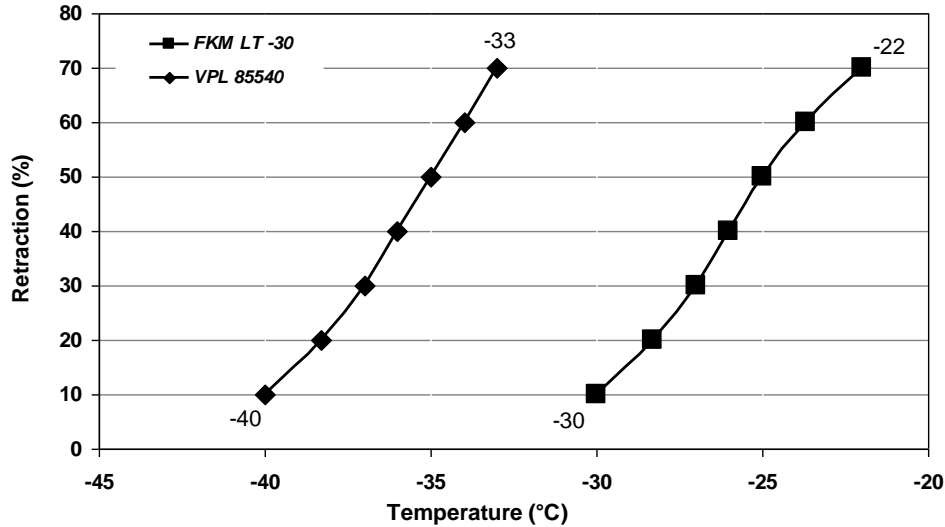


Figure 2: Temperature retraction curves of MOVE-based FKM (VPL 85540) vs. FKM LT -30.

The new generation of fluoroelastomers, based on MOVE technology, are commercialized as VPL grades.

DISCUSSION

The properties of new fluoroelastomers made with the MOVE monomer are shown in the following section. Testing includes dynamic mechanical analysis (DMA), low temperature properties, fluid resistance, and compression stress relaxation tests (CSR). Testing compares FKM VPL 85540 (T_g - 41°C) with conventional ASTM D1418-05 FKM type 3, low temperature, peroxide curable polymer (T_g - 33°C), other common oilfield fluoroelastomers, and a low temperature hydrogenated nitrile butadiene rubber (HNBR/17% ACN, T_g -40°C,) elastomer.

Low Temperature Properties

A characterization of FKM VPL 85540 was completed via DMA and it was compared to standard FKM LT -30, LT HNBR and TFE/P FEPM polymer. The DMA tested compounds each had hardness values in a range of 70 ShA.

The following graph (see figure 3) reports the storage (shear) modulus G' versus temperature curves for all the samples. The huge decrement (two orders of magnitude) of G' corresponds to the T_g of the polymers. Thus, DMA curves can provide useful information about the service temperature of the elastomers. The T_g corresponds to the point when rubbery, elastic behavior changes to the glassy state as all large scale polymer chain movement stops as the temperature is lowered. This loss of elasticity results in the reduction of sealing stress and a seal will take on permanent set.

It can be noted that FKM VPL 85540 provides the same low temperature performance as the HNBR LT and an expanded low temperature capability in comparison to the standard fluoroelastomer LT -30 °C. TFE/P elastomer is well known for its high T_g that makes this polymer unsuitable for applications in cold environments.

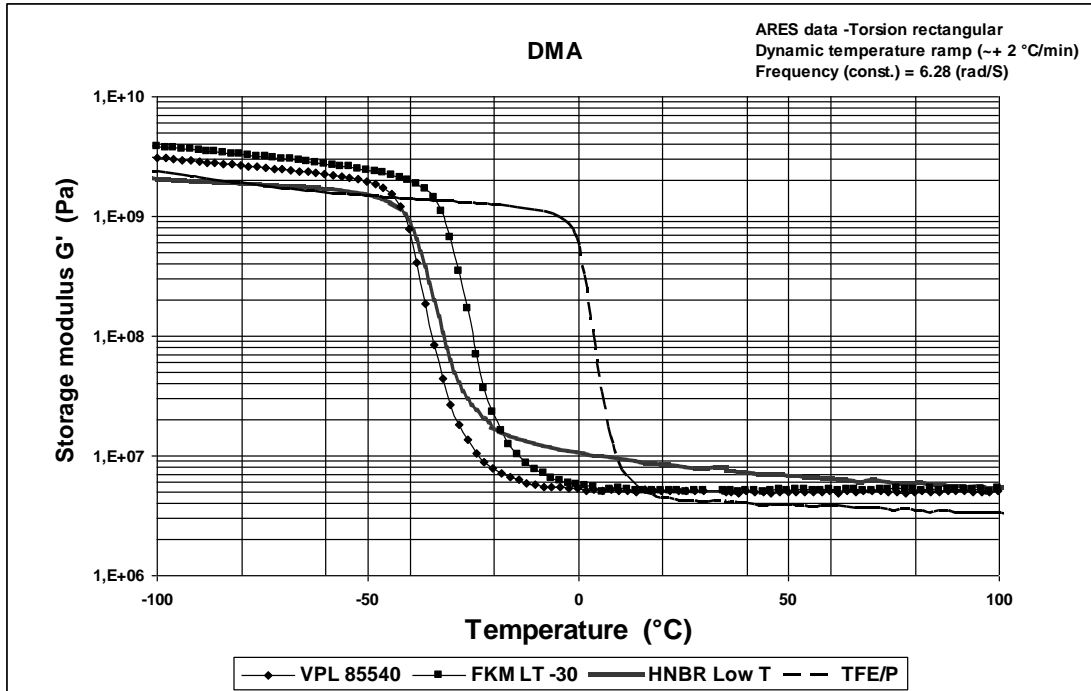


Figure 3: Dynamic Mechanical Analysis of the new VPL 85540, standard type 3 FKM with Tr10 -30°C (FKM PL 855), HNBR for low temperature applications and TFE/P FEPM elastomer.

Retraction at Low Temperature

Another test to characterize the low temperature profile of an elastomer is the Temperature of Retraction (Tr Test), ASTM D1329. The Tr10 is the temperature at which a stressed sample can recover the 10% of the original stress. Tr10 value is often few degrees more than the T_g . In the table below, we report the Tr10 values of the same polymers used for the above DMA.

	VPL 85540	HNBR	LT FKM	TFE/P
Tr10 (°C)	-40	-37	-30	+3

Table 1: Tr10 values of VPL 85540, LT HNBR, FKM LT-30, and TFE/P elastomer.

Fluid Resistance

Methanol injection in high concentrations can be necessary to prevent hydrate formation in gas production. Hydrates can damage equipment and block flowlines, thereby making pure methanol resistance an important material characteristic for seals utilized in the injection systems. It is a well known phenomenon that methanol will significantly swell type 3, low temperature fluoroelastomers containing PMVE with T_g -33°C. Volume swell in excess of 40% combined with significant changes to hardness and mechanical properties are observed in 100% methanol (see figure 4). This high volume swell renders the material unsuitable for use in methanol sealing applications. Dilution of methanol by water can reduce the volume swell. However, in HPLT conditions with long flowlines continuous injection of high concentrations of methanol may be necessary.

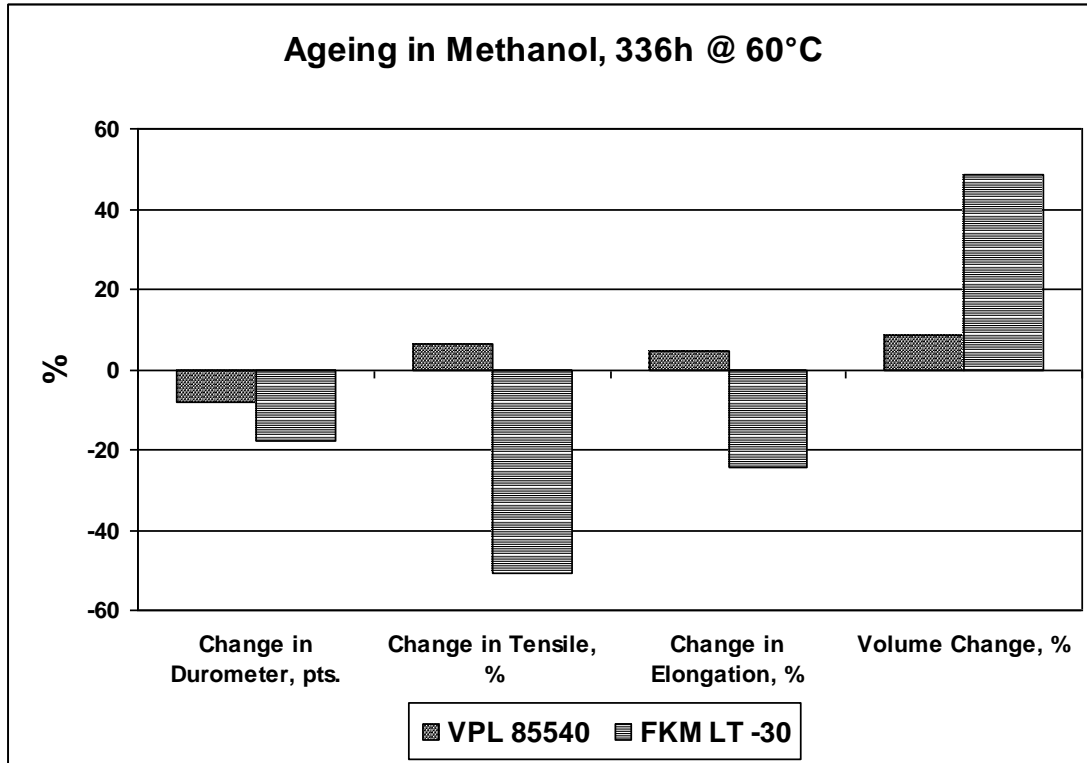


Figure 4: Methanol ageing 336 hours @ 60°C: comparison of VPL 85540 versus FKM LT-30. The new VPL grade show superior chemical resistance, not only in terms of volume swell, but also in terms of retained mechanical properties.

The use of MOVE monomer in FKM VPL 85540 alters the observed trend of high methanol swelling as low temperature performance improves. LT HNBR elastomers are available with T_g near -40°C and offer an alternative low temperature solution with good methanol resistance. However in order to achieve this degree of low temperature performance, the overall fluid resistance is compromised by a low acrylonitrile (ACN) content as can be observed by the volume swell in toluene (see figure 5). Fluoroelastomers based on TFE/P also possess the same combination of fluid resistance characteristics as LT HNBR when considering methanol and toluene. As the T_g of TFE/P polymers is extremely high (+3°C), this type of fluoroelastomer is not suitable for HPLT applications.

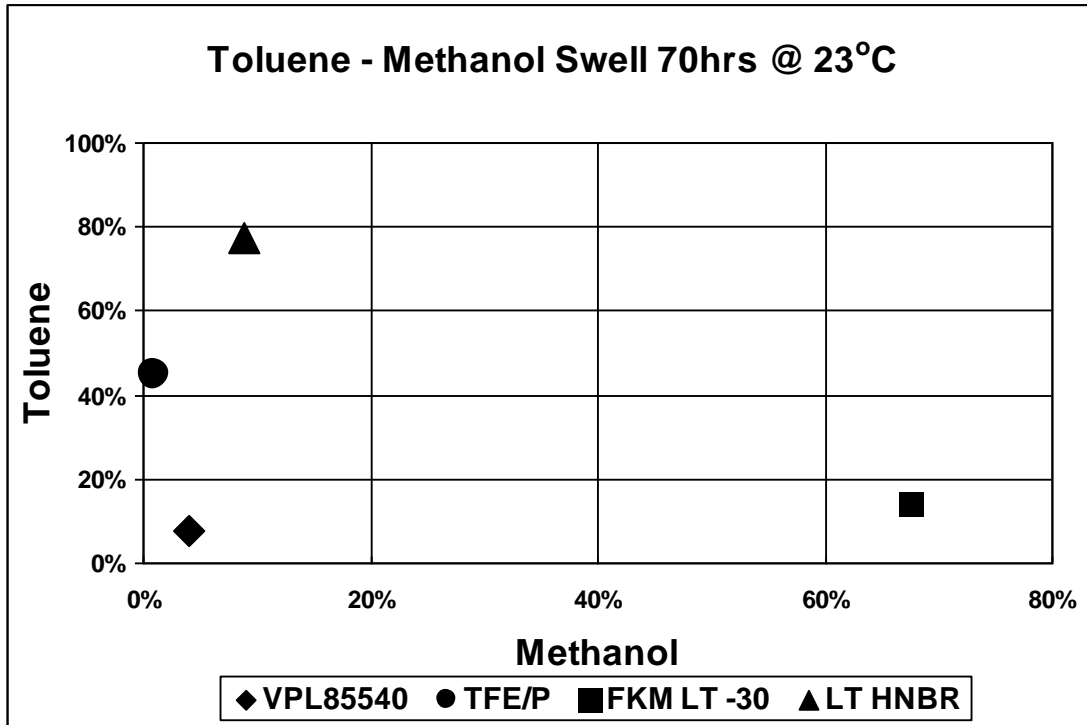


Figure 5: Volume swell in toluene versus methanol at 23°C: VPL 85540, FKM LT-30, TFE/P and LT HNBR.

Crude oil is a complex mixture of different hydrocarbons such as alkanes, cycloalkanes and aromatic hydrocarbons which need to be handled during upstream and downstream operations. Resistance to Iso octane and the reference NORSOK^{xi} test fluid¹ is very important in this context. Toluene is representative of aromatic hydrocarbons.

Both FKM VPL 85540 and type 3, low temperature fluoroelastomers containing PMVE with T_g -33°C show excellent resistance to swelling in the different hydrocarbons compared to LT HNBR and TFE/P elastomer types (see figures 6 and 7). It is important to recognize that excessive swelling, and the resultant loss in hardness, of an elastomer seal can lead to the extrusion of the seal as the housing groove becomes overfilled leading to premature seal failure. This situation worsens if the seal experiences high pressure during operation. In certain cases a small amount of volume swell can be positive and increase the retention of sealing force but values above 20% are generally considered to be too high for a seal to be effective^{xii}. FKM VPL 85540 retains its hardness (see figure 8) after immersion in the range of fluids tested.

¹ Simulated production fluid for sweet service conditions, minus water and gas content.

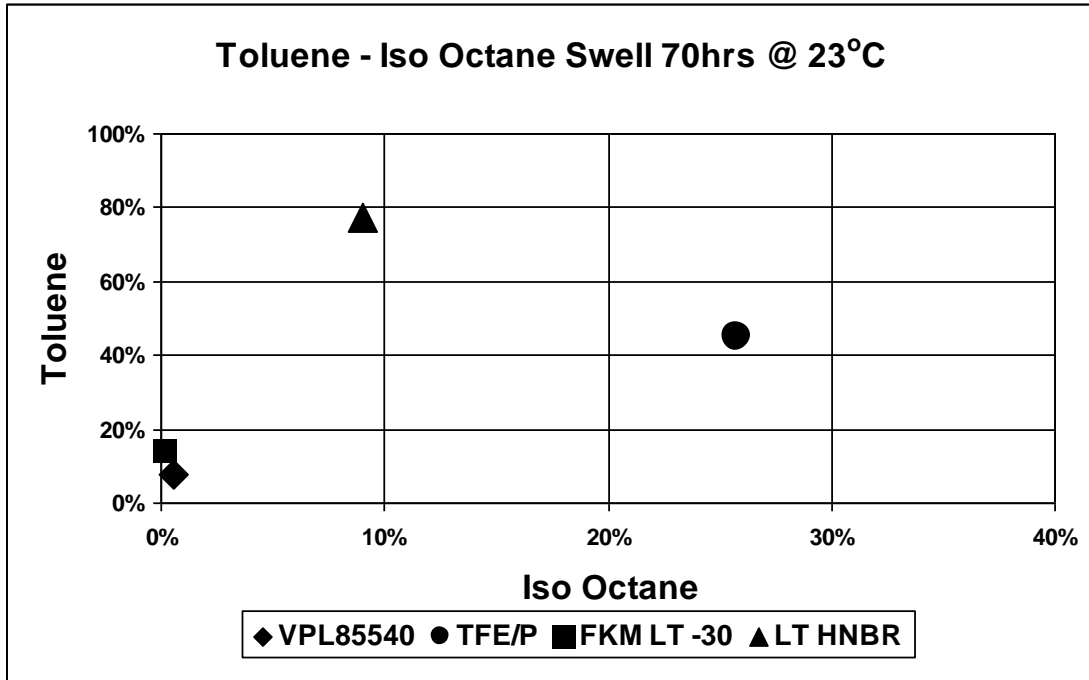


Figure 6: Volume swell in toluene versus Iso octane at 23°C: VPL 85540, FKM LT-30, TFE/P and LT HNBR.

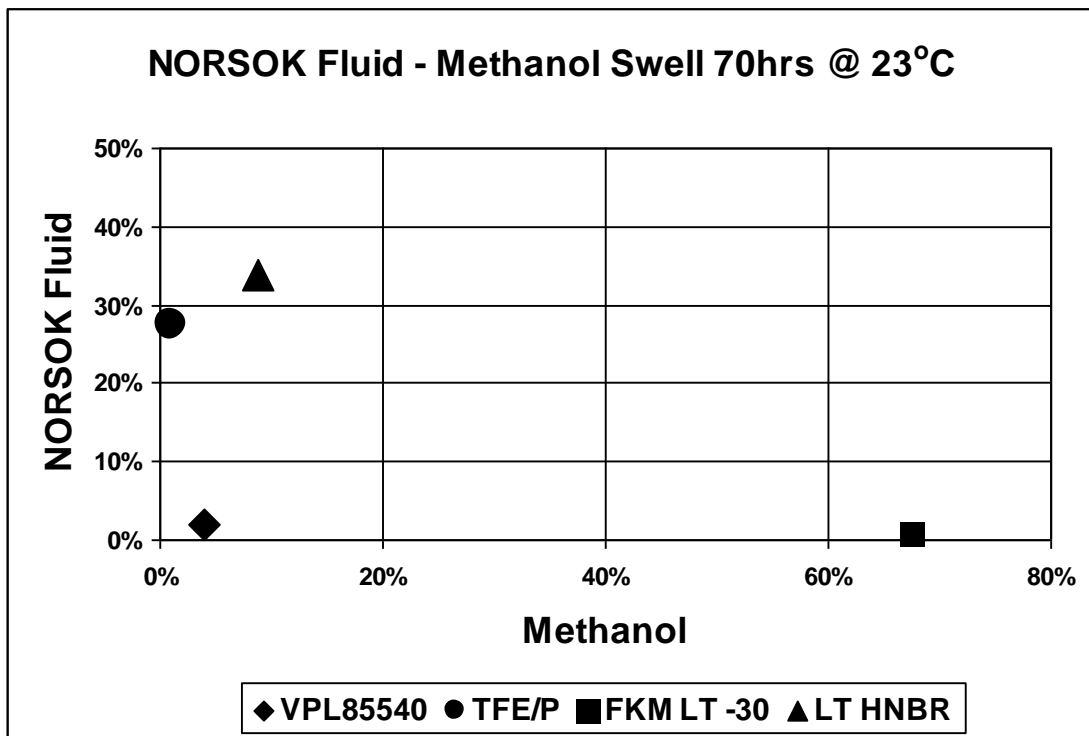


Figure 7: Volume swell in NORSOK fluid (70% heptane/ 20% cyclohexane/ 10% toluene) versus methanol at 23°C: VPL 85540, FKM LT-30, TFE/P and LT HNBR.

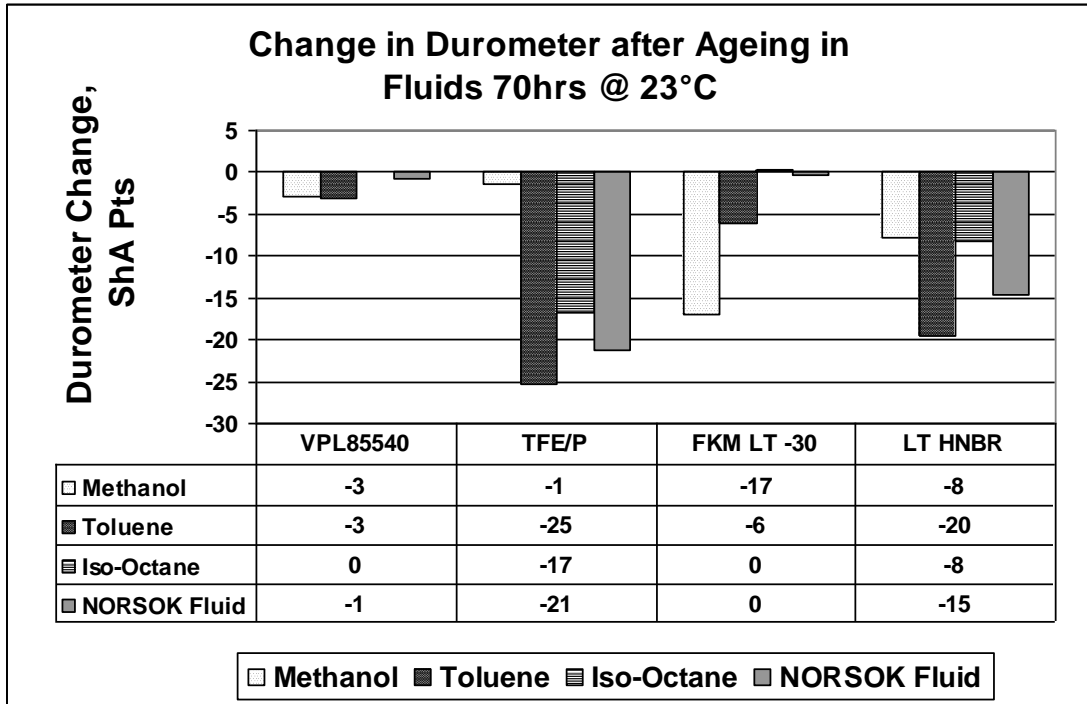


Figure 8: Change in durometer after ageing in methanol, toluene, iso octane and NORSOK fluid 70 hrs at 23°C: VPL 85540, FKM LT-30, TFE/P and LT HNBR.

Thermal and Mechanical Properties

FKM VPL 85540 can be compounded very simply and cured via a peroxide system. Addition of fillers such as carbon black will increase tensile strength and modulus values. Base physical properties comparing type 3, low temperature FKM to FKM VPL 85540 are recorded in Table 2. The compounds are not optimized for a specific application but are compounded to 90 Shore A which is typical for many oilfield applications. Alternative formulations and fillers may be used to modify the physical properties for different applications and seal geometries.

Formulations:		FKM LT -30	VPL 85540
Polymer		100	100
Peroxide DBPH (50%)	phr	2	2
TAIC DLC A	phr	4	4
N 330 Carbon Black	phr	25	25
MT N 990 Carbon Black	phr	30	30
Physical Properties: Press cure, 10' @ 177°C, Post Cure: 4 h @ 230°C			
Hardness	ShA pts	88	90
Tensile Strength	psi	2775	1835
Elongation at Break	%	110	89
Modulus @ 50%	%	796	894
Tear, Die C	ppi	146	107
Physical Properties @ 163°C:			
Change in Tensile from RT	%	-67	-50
Elongation at Break	%	88	54
Change Elongation at Break from RT	%	-22	-27
Change in M50 from RT	%	-34	-35
Tear, Die C	ppi	56	48

Compression Set, ASTM D 395B, Plied Disks			
70 h @ 200°C	%	29	34
336 h @ 177°C	%	23	42
Heat resistance, ASTM D573, 1500 h @ 200°C			
Change in Durometer	ShA pts	+4	+2
Change in Tensile	%	-41	-16
Change Elongation at Break	%	-13	+4
Change in M50	%	+19	-6

Table 2: Physical properties and heat ageing of two high durometer compounds based on VPL 85540 and FKM LT-30.

As detailed earlier in the paper, VPL 85540 provides an extended low temperature service range. However the greater benefit to the seal designer is to have a material that has an extended performance range for both high and low temperature applications and create more durable equipment.

A closer examination of the thermal stability of VPL 85540 plots the change elongation at break with time. FKM VPL 85540 exhibits the typical long term heat stability of FKM as demonstrated by retained elongation. Importantly, MOVE monomer technology does not compromise the thermal stability property of FKM (see figure 9).

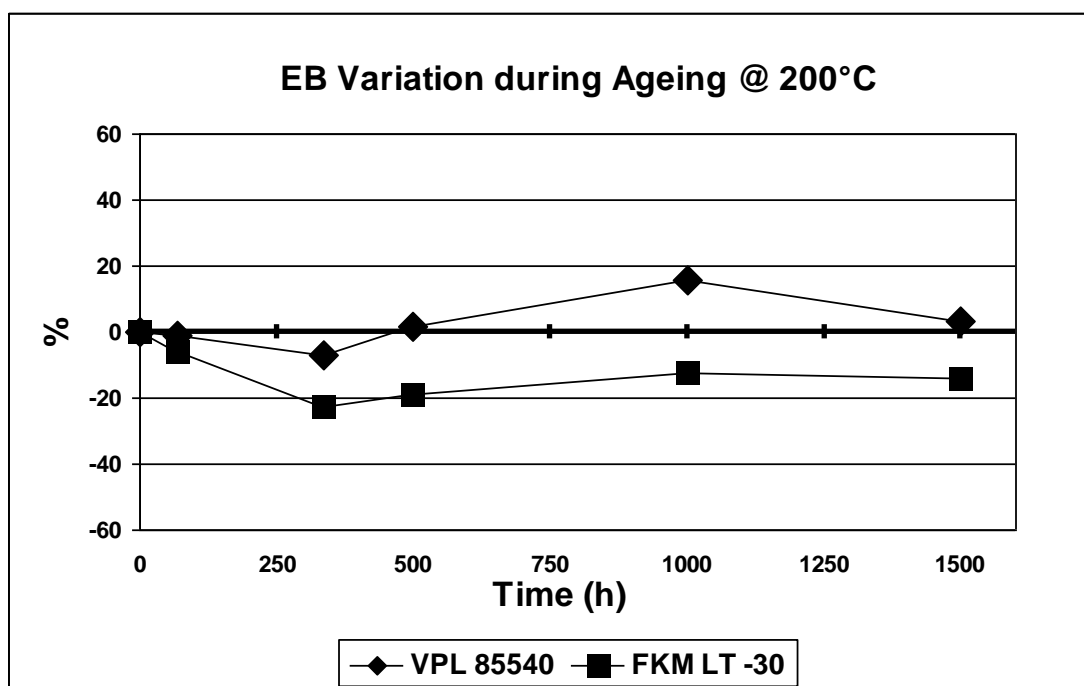


Figure 9: Variation of elongation at break from initial values during ageing at 200°C.

While VPL 85540 shows long term heat resistance by retained elongation break, it is also important to investigate the retained sealing property of the material for use in a seal or o-ring application. Chemical changes through oxidation induced processes such as elevated temperatures can cause the loss of sealing force as the elastomer relaxes and can be measured with compressive stress relaxation testing (CSR). CSR charts are limited down to 50% of retained sealing force; data recorded below this line are usually neglected due to degradation of the material^{xiii}.

Long term CSR testing with FKM LT -30 shows that VPL 85540 retains its sealing force similar to the standard technology FKM (see figure 10). The stability of fluorine based elastomers is superior in high temperature performance to LT HNBR (see figure 11). CSR data demonstrates the excellent sealing behavior of FKM VPL 85540 in high temperature environments.

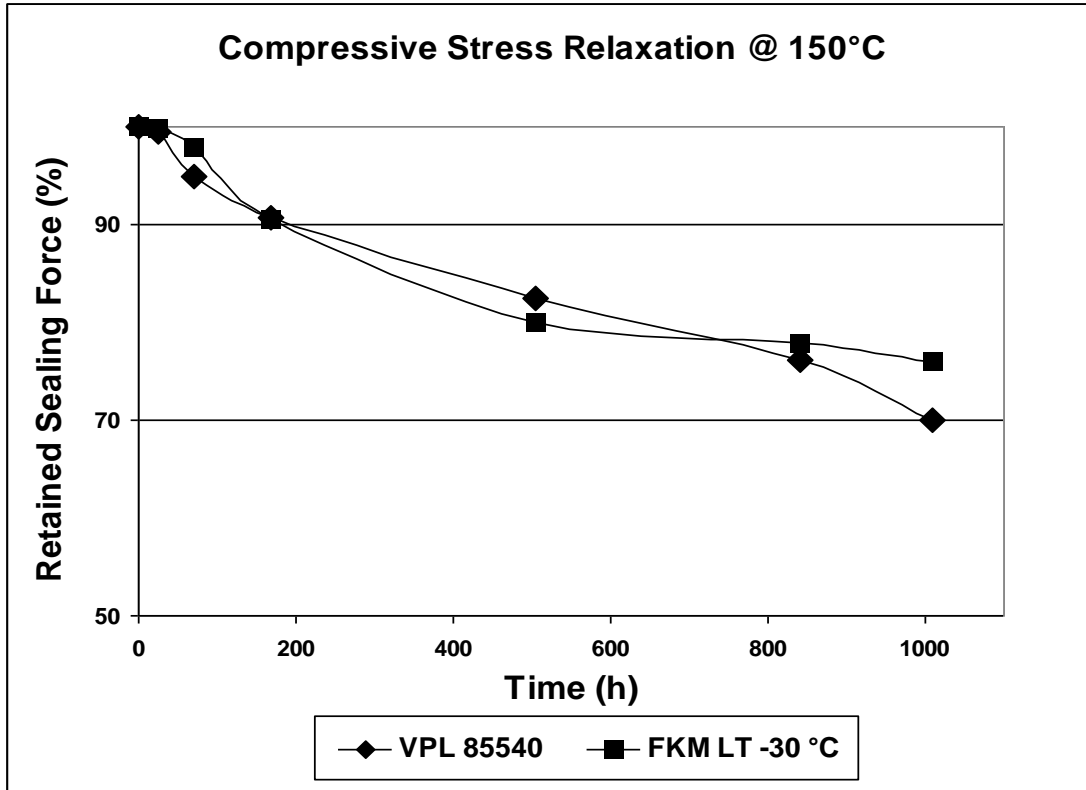


Figure 10: Long term retained sealing force versus time at 150°C of VPL 85540 compared to standard Low Temperature FKM. The introduction of MOVE monomer has not affected the long term sealing behavior as the trends between the two polymers are similar. CSR measurement using GM test jigs^{xiv} reference ASTM D6147-97(2008) and measurement readings taken after 1 hour cool @ 23°C

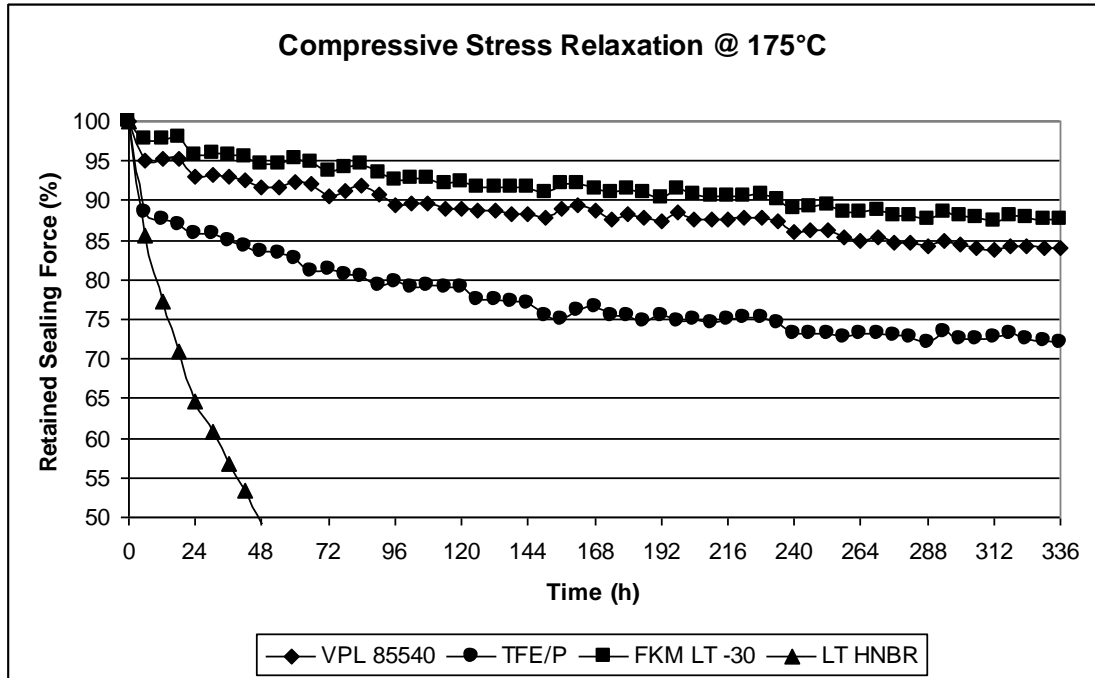


Figure 11: CSR plot using Elastocon EB01HT test instrument at 175°C on size #214 o-rings as an alternate CSR test method to figure 10. LT HNBR lost sealing force after 48 hours at the elevated temperature. VPL 85540 and FKM LT -30 retained their sealing force best among the fluorinated elastomers with TFE/P showing a faster decline in sealing force retention.

CONCLUSION:

The new type of fluoroelastomer using MOVE technology allows for the creation of polymers that exhibit the properties of an extended low temperature performance range, good compression set, and heat resistance. FKM VPL 85540 has significantly improved fluid resistance compared to the standard -30°C low temperature FKM technology. In particular, FKM VPL 85540 has low volume swell in methanol, whereas the standard -30°C FKM exhibits very high volume swells in methanol limiting its application range in certain aggressive environments.

Compared to TFE/P based elastomers, FKM VPL 85540 shows an improvement of 45°C in low temperature performance. It also has much lower swell in hydrocarbons, particularly in aromatics, than TFE/P based elastomers. FKM VPL 85540 adds a level of safety and capability for equipment that may be installed in applications where fluids may change over the field or process lifetime.

HNBR elastomers are commercially available with Tr10 values close to -40°C. However in order to achieve this degree of low temperature performance, the fluid resistance of normally associated with HNBR is compromised by a low ACN content. FKM VPL 85540 has superior sealing behavior at elevated temperature, wider service temperature range, and better hydrocarbon resistance compared to low temperature HNBR.

In summary, VPL polymers and MOVE monomer technology has enabled the balance between thermal properties, fluid resistance and high / low temperature sealing behavior to be optimized. Among the elastomers tested, VPL 85540 has the broadest temperature performance range and fluid resistance. In the future these capabilities will allow the seal and equipment designer to create new tool designs, and utilize sealing strategies previously not possible with existing elastomer technology.

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