Consumer Solutions

FSRs in Extreme Applications

Proof of the New Paradigm

Fluorosilicones for Demanding Applications

For more than 50 years, fluorosilicone elastomers have been used in demanding applications where fuel resistance, low-temperature performance and high-temperature performance are required. Beginning with their use in the aerospace industry and followed by their expansion into automotive applications, fluorosilicone polymers have always been considered a premium, high-priced product. Recognizing the financial realities of today's automotive markets, Dow has tapped into its extensive knowledge of fluorosilicone chemistry and compounding expertise to create a new family of high-value, specific compounds. These have a good balance of fuel and oil resistance and mechanical properties over a wide range of temperatures.

Now, for EXTREME Applications

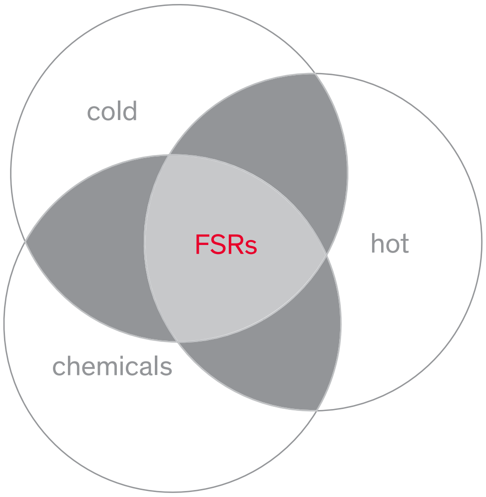
This white paper describes the high-performance capabilities of both bases and the latest appropriately priced SILASTIC™ and XIAMETER™ fluorosilicone compounds from Dow in terms of:

- Oil and fuel resistance
- Mechanical properties
- Abrasion resistance

And in doing so, this paper opens the door to competitive advantages for innovative manufacturers of seals, diaphragms and other high-performance rubber parts.

A Dow Publication

This paper contains conclusions derived from laboratory tests conducted by the independent plastics and rubber test facility Rapra Technologies. This research was sponsored by Dow. As a leading supplier of fluorosilicone rubber for use in extreme applications, Dow regularly sponsors such research – both internally and externally. This book also contains additional non-Rapra Technologies test data, as indicated. Publications such as this are intended to help the rubber and plastics industry as a whole develop higher-performance and more cost-effective solutions.



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The Proof of the New Paradigm

1. In all cases, the tear strength at 200°C (392°F) of the two FSR compounds is significantly higher than the FKM compounds.
2. The elongation at break for the FSR compounds at 200°C is significantly better than any of the FKM compounds evaluated as part of this test program.
3. The two FSR compounds have tensile strength values at 200°C similar to those of FKM compounds.
4. FSR compounds generally have a wider operating temperature range compared to FKM compounds due to their lower glass transition temperatures.
5. For high-temperature applications (up to 200°C), FSR elastomers compare favorably with FKM materials in terms of tensile and tear strength.

The New Paradigm

You are about to witness a global switchover in extreme applications.

From: HNBR, XNBR, Urethane, FKM, ACM and AEM

To: FSR[1]

Why? Because FSRs offer:

- An opportunity to improve current products
  - Increased temperature ranges
  - Increased lifetime
  - Increased part-design options
- More freedom in new product concepts
  - Smaller parts
  - Reduced energy of operations
- A chance to reduce costs
  - Faster curing
  - Reduced handling costs

The Proof of the New Paradigm

This white paper provides the quantitative laboratory test conclusions and the qualitative situation analysis that shows why the switchover will happen. Companies among the first in the switchover process will seize a powerful commercial advantage.

Independent Laboratory Test Findings

In 2003, Dow commissioned Rapra Technologies to compare two FSR compounds[2] against three leading FKM compounds[3].

Although Rapra Technologies does not recommend materials for specific applications, the following findings clearly support the increased use of FSRs in extreme temperatures and mechanical performance applications.

Rapra Technologies is Europe's leading independent plastics and rubber consultancy. Rapra provides comprehensive consultancy, technology and information services for the polymer industry and industries using plastics and rubber in any component, product or production process.

Where Did FSRs Come From?

In the 1950s, Dow decided to upgrade its popular SILASTIC™ dimethyl silicone rubber known as VMQ. This was in response to the anticipated need for rubbers with increased solvent resistance in extreme applications. The resulting upgrade was fluorosilicone rubber, known as FSR.

The trifluoropropyl-substituted silicone polymers (which gave the rubbers a significant increase in fuel and chemical resistance) were first synthesized in the laboratory by Dow researcher Dr. Ogden Pierce and his coworkers. They substituted a fluorocarbon moiety for the methyl hydrocarbon group. Dow then commercialized the process.

Continuous Improvement

As automotive and aerospace manufacturers developed increasingly higher-performance systems, it was clear that higher-performance FSRs would be needed. This need was anticipated and

Table 1: Continuous improvement in the physical properties of FSRs

	SILASTIC™ LS-40 Fluorosilicone Rubber	SILASTIC™ LS-2840 Fluorosilicone Rubber	SILASTIC™ LS 5-2040 Fluorosilicone Rubber
Introduced	1950s	1970s	1990s
Tensile, MPa (psi)	5.5 (797)	10.1 (1468)	12.4 (1800)
Elongation	271	519	550
Tear, die B, kN/m (ppi)	12 (66)	30 (166)	40 (220)
Shore A durometer	41	38	40

These high-performance elastomers exhibit little change in properties over a wide temperature range.

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[1] FSR: Fluorosilicone Rubber, also known as FVMQ.

[2] SILASTIC™ LS-2860 Fluorosilicone Rubber and SILASTIC™ LS 5-2060 Fluorosilicone Rubber from Dow were used in the test FSR compound.

[3] Industry-leading FKMs were used in the three comparative compounds. See page 6 for the generic formulations.

met with a continuous improvement in FSR technology, which saw the doubling of FSR tensile strength and elongation characteristics and a four-fold increase in tear, die B – as shown in Table 1. This illustrates the typical mechanical properties for three different generations of fluorosilicone rubber bases. The first low-swell (LS) materials were developed in the 1950s. While they exhibited modest properties, the next generation of low-swell fluorosilicone materials such as SILASTIC™ LS-2840 Fluorosilicone Rubber showed significant improvements. Dow's next addition to the base product line, typified by SILASTIC™ LS 5-2040 Fluorosilicone Rubber, exhibit strength and tear properties approaching that of many of the organic rubbers at room temperature and exceeding the properties of most organic rubbers at elevated temperatures.

The Paradigm Shift

In addition to the improvement in mechanical properties, the abrasion resistance of high-tear FSRs is now better than FKM compounds – as measured by Taber abrasion. In 2002, C.A. Sumpter[1] addressed the undeserved perception that the abrasion resistance of VMQ materials is low. In Table 2, the abrasion resistance of VMQ was verified and extended to include several FSR materials. The SILASTIC™ rubbers from Dow were peroxide-cured.

Table 2: Taber abrasive testing of FKM, standard FSR and VMQ rubbers

Compound	Average Loss, mg/cycle
XIAMETER™ RBB-2002-50 Base	0.0216
SILASTIC™ LS 5-2040 Fluorosilicone Rubber	0.0301
Peroxide-cured unfilled FKM	0.0483
SILASTIC™ LS-2840 Fluorosilicone Rubber	0.0830
Bisphenol-cured filled FKM	0.1089

Test conditions: 72 rpm, 5000 cycles, H-18 wheels, 1000 g load

Test Results

Pages 5 to 8 show the main results and conclusions from the laboratory tests conducted by Rapra Technologies.

FSR-based compounds

Material	Batch 1	Batch 2
SILASTIC™ LS 5-2060 Fluorosilicone Rubber		100
SILASTIC™ LS-2860 Fluorosilicone Rubber	100	
XIAMETER™ RBM-9002 Rubber Additive	1	1
Varox DBPH-50	1	1

FKM-based compounds

37V: A bisphenol-cured dipolymer based on 66% fluorine dipolymer

Ingredient	Level (phr)
66% fluorine dipolymer	100.0
MT N990 carbon black	30.0
Maglite DE	3.0
Sturge VE	6.0
Viton Curative 50	2.5

38V: A bisphenol-cured terpolymer based on 68% fluorine terpolymers

Ingredient	Level (phr)
68% fluorine terpolymers	100.0
MT N990 carbon black	30.0
Maglite DE	3.0
Sturge VE	6.0
Viton Curative 50	2.5

39V: A peroxide-cured terpolymer based on 67% fluorine terpolymer manufactured utilizing the latest technology

Ingredient	Level (phr)
70% fluorine	100.0
MT N990 carbon black	30.0
Zinc oxide	3.0
TAIC	3.0
Luperox 101-XL	3.0

The news, and now proof, that FSR materials have good abrasion resistance opened a major door of opportunity: the application of fluorosilicone compounds in dynamic seals such as sliding shaft seals and rotating seals.

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[1] Sumpter, C.A., "Silicone for Use in Abrasion Resistant Applications"; International Silicone Conference: Akron, OH, 2002.

Variation in Tensile Strength with Temperature

The tensile strength data are presented with the error bars representing one standard deviation of the results about their mean. Tests were conducted by Rapra Technologies.

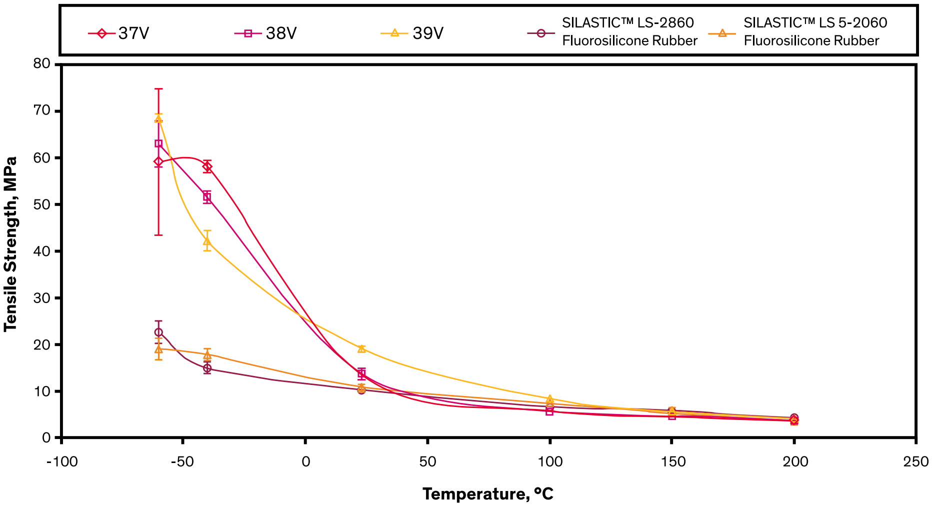
The variation in tensile strength with temperature follows the expected fall with increasing temperature. Also, the drop follows an approximately exponential curve – at least over the temperature range examined in this study. The three fluorocarbon compounds show a much greater temperature effect (especially at the low temperatures) than the fluorosilicone compounds, which have much flatter responses in general. The fluorocarbon compounds tend to have higher glass transition temperatures, so a large increase in strength is to be expected.

Variation in Elongation at Break with Temperature

The elongation at break data are presented with the error bars representing one standard deviation of the results about their mean. Tests were conducted by Rapra Technologies.

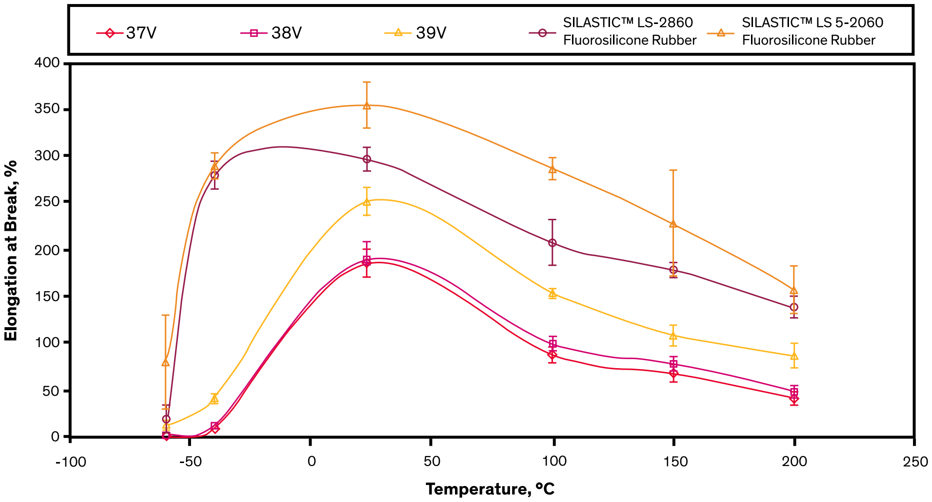
For elongation at break, the three fluorocarbons that have glass transition temperature (T_g) above -20°C show the expected rapid loss in elongation at break as the temperature is lowered through the glass transition point. This loss in elongation at break for FSR does not occur until temperatures fall to -50°C. The same is true for those compounds having T_gs in this region. It is also noticeable that the compounds with the lowest T_gs and the least variation in tensile strength[1] and elongation at break with temperature are also those with very broad tan delta curves in the dynamic mechanical properties. Clearly, these are related phenomena.

Figure 1: Variation in tensile strength with temperature



The fluorosilicone compounds (using SILASTIC™ LS-2860 Fluorosilicone Rubber and SILASTIC™ LS 5-2060 Fluorosilicone Rubber) have tensile strength values at 200°C, similar to the fluorocarbon compounds.

Figure 2: Variation in elongation at break with temperature



The 'elongation at break' figures of the fluorosilicone compounds (using SILASTIC™ LS-2860 Fluorosilicone Rubber and SILASTIC™ LS 5-2060 Fluorosilicone Rubber) at 200°C are significantly better than the fluorocarbon compounds.

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[1] Tan delta is the ratio of the loss modulus to the elastic modulus. In a single numeral, it represents the elastomer's ability to absorb and return the energy exerted during deformation. A broad tan delta peak over a wide temperature range indicates that the mechanical properties change little over that temperature range. This is desirable for consistent operation while experiencing varying conditions.

Variation in 100% Modulus with Temperature

The 100% modulus data are presented with the error bars representing one standard deviation of the results about their mean. Tests were conducted by Rapra Technologies.

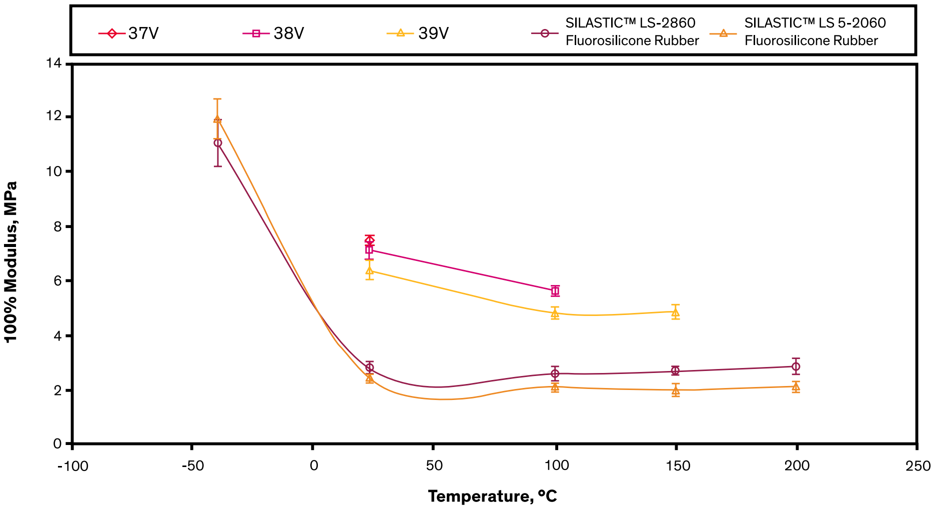
The 100% modulus graph is more sparse than the other tensile properties because the temperature range over which the elongation at break exceeds 100% is limited. There is a significant difference in modulus level for the three fluorocarbons compared to the fluorosilicones at ambient temperature and above, and the temperature range over which this modulus exists is also much narrower for the fluorocarbon compounds.

Variation in Tear Strength with Temperature

The graph below shows how each compound's tear strength varies with temperature. Generally, tear resistance is weaker at high temperatures and stronger at low temperatures. However, at around 0°C this trend seems to reverse (i.e., tear strength starts getting weaker as temperatures reduce). Tear strength variation in the FKM compounds becomes large as the rubber approaches its glass transition point at low temperatures. Tests were conducted by Rapra Technologies.

The distinctions between the two classes of fluorine-containing elastomers are less clear-cut for tear strength than they were for tensile properties. Certainly, the FSRs show broadly similar temperature sensitivities to those of the fluorocarbons, and there is less separation of the two families into distinct groupings.

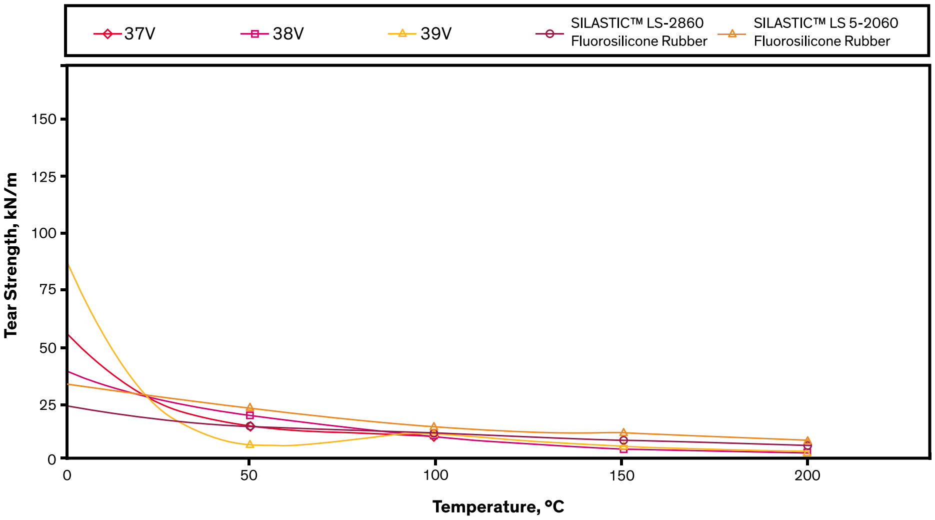
Figure 3: Variation in 100% modulus with temperature



The hardness of the compounds (at room temperature) is reflected in the levels of modulus at this temperature, with the harder compounds showing the higher modulus levels.

Note: For the test compound 37V, there is no curve. This is because the elongation at break for 37V only reaches 100% at one of the selected temperatures: 23°C.

Figure 3: Variation in tear strength with temperature



In all cases, the tear strength at 200°C of the fluorosilicone compounds (using SILASTIC™ LS-2860 Fluorosilicone Rubber and SILASTIC™ LS 5-2060 Fluorosilicone Rubber) exceeds that of the fluorocarbons.

Realizing the Opportunity

The previous pages have shown that FSR materials offer good abrasion resistance and offer many opportunities to create new, more cost-effective, high-performance elastomer solutions for extreme applications. But how do you realize those opportunities? That's where Dow can help, with the expertise to optimize formulations and develop the exact elastomer solution for your application. This is possible because Dow operates a unique, combined service: base formulation technology and compounding expertise, via its global centers of expertise. More information can be found on the Dow website at **consumer.dow.com**.

This compounding expertise has led to many successful products that satisfy specific customer needs while delivering the EXACT properties required to be competitive in their marketplace.

Some examples of problems that have been solved through Dow compounding technology are:

- Reducing the damage to parts during assembly by developing a proprietary lubricity additive
- Reducing the permeation in uncompressed FSR for a turbocharger hose inner liner
- Simplifying processing by modifying the Mooney viscosity, plasticity and handling properties of the FSR
- Increasing the productivity of injection molding machines (with minimized interruptions) by incorporating a special mold-release agent
- Reducing scrap by improving the hot tear properties of complex shapes and undercut molds, which made their removal easier
- Dramatically reducing cycle times (to less than two minutes) with rapid-cure formulations
- Increasing the speed of automated parts production with a fluorosilicone/dimethyl silicone liquid rubber

Maximizing Rubber Fabrication Value

A compounding method to help maximize the value of the rubber fabrication is to use extending fillers. The addition of extending fillers typically results in reduction of mechanical properties; however, by using high-tear/high-strength bases, adequate physical properties are retained to meet the needs of several applications. Of course, FSR with extending fillers still retains the excellent low-temperature properties, as well as the chemical and fuel resistance of the unfilled starting elastomer. As you can see by the red line in Figure 5, the average volume swell for an 80/20 (FSR/VMQ) blend with 60 parts of an extending filler is less than 30% in the fuel. Use of appropriate extending filler can significantly improve fuel swell properties while lowering cost.

Figure 5: Effect of changing the weight percentage of FSR on volume swell in fuel and oil

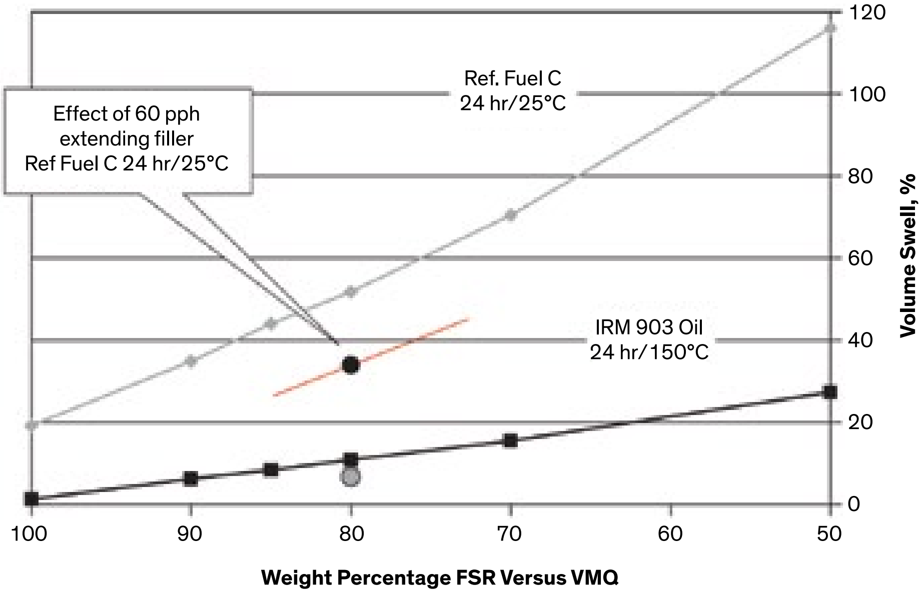


Table 3: Effect of different fillers on FSR properties

	Base Alone	Filler 1	Filler 2	Filler 3
Tensile, MPa (psi)	12.7 (1844)	7.0 (1013)	6.1 (884)	4.8 (698)
Elongation, %	589	148	235	305
100% modulus, MPa (psi)	0.9 (131)	6.5 (937)	3.5 (508)	1.9 (279)
Tear, die B, kN/m (ppi)	45 (249)	18 (102)	25 (140)	26 (142)
Shore A durometer	42	78	65	64
Resiliency	19	16	15	14
Specific gravity	1.45	1.75	1.77	1.69
C/S 22 hr/177°C (350.6°C), %	10.4	32	19.3	59.2

Post-cured properties of highly filled FSR. Combinations of these and other fillers can provide tailored mechanical properties at attractive prices compared to FKM and other high-performance elastomers.

Balanced Properties and Reduced Costs

Comparison between the FKM and the FSRs illustrates the advantages of using FSR/VMQ blends as opposed to pure FSR or pure FKM. Formulations based on SILASTIC™ LS 5-2040 Fluorosilicone Rubber and SILASTIC™ LS 5-2060 Fluorosilicone Rubber indicate good resistance to most conditions in both oils. However, using a blend of FSR and VMQ elastomers results in both balanced properties as well as reduced cost in the application.

All five formulations shown in Figure 6 are specific to the diesel turbocharger hose inner liner application. In this application, resistance to two different synthetic lubricants as well as diesel fuel is needed to meet the longevity requirements of this critical performance part[1].

FKM 1 and FKM 2 are specifically formulated for the turbocharger hose application and provided without comment by companies actively engaged in the development of this part. The comparison was performed in Dow laboratories.

A Choice of Performances from a Choice of Compound Prices

Figure 6 shows performance comparisons of FKMs and FSRs in a specific application: a turbocharger hose. The comparison shows how a choice of performances is available with the consequent choice of compound prices.

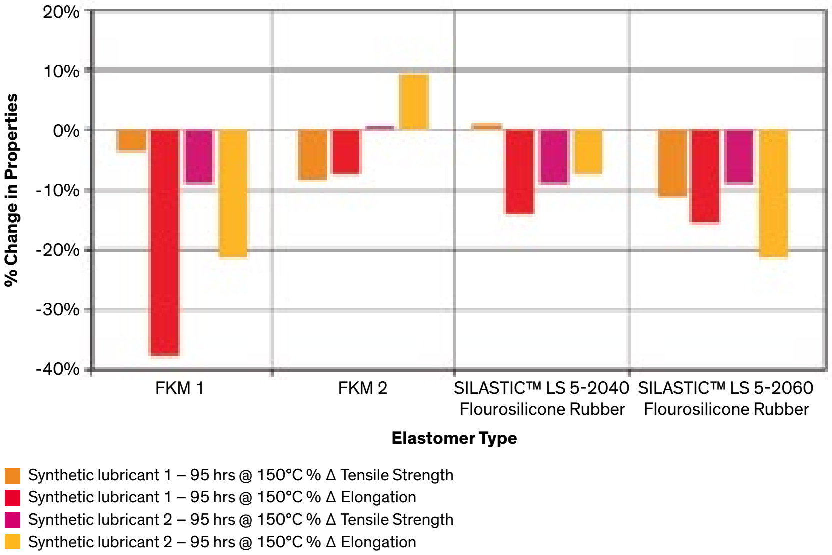
Achieving the EXACT Specification

FSR compounds are cost-effective because they are designed to meet specifications.

Customized compounds can provide the EXACT set of mechanical properties, as well as a manufacturing processing profile needed for cost-effective utilization of FSR.

More than 20 different types of SILASTIC™ fluorosilicone bases are available for compounding. By uniting SILASTIC™ FSR/VMQ bases with Dow's compounding technology, a wide range of elastomeric properties can be achieved. This is illustrated in Table 4 and Figure 5, where blends of FSR and dimethyl silicone can be used to economically eliminate oil weep in engine seals.

Figure 6: Comparison of turbocharger hose formulations



PLEASE NOTE: The test results above concern compounds designed for the specific application of turbocharger hose. These are not the same compounds used by Rapra Technologies for their tests. Rapra used generic compounds for general comparisons. Those compound formulations and test results are shown on pages 5 to 8.

Table 4: Physical properties of FSR/VMQ blends

		FSR/VMQ Weight Ratio					
Test	**Unit**	**100/0**	**90/10**	**85/15**	**80/20**	**70/30**	**50/50**
Tensile	psi	1867	1723	1557	1637	1578	1518
	MPa	12.9	11.9	10.7	11.3	10.9	10.5
Elongation	%	513	481	453	453	445	429
100% modulus	psi	137	177	191	211	229	243
	MPa	0.9	1.2	1.3	1.5	1.6	1.7
Tear, die B	ppi	250	265	259	208	210	116
	k N/m	45.0	47.7	46.6	37.4	37.8	20.9
Shore A durometer		42	47	48	50	52	53
Resiliency		20	23	25	27	32	41

A range of performance in oil and fuel is available without sacrificing mechanical properties.

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[1] 2001-01-1124 SEA paper "Performance in diesel and biodiesels of flourosilicone materials used for automotive quick connector fuel line o-rings and other sealing applications"; Tim Maxon, Bill Logan, Shona O'Brien.

The results in Table 4 demonstrate that good physical properties are maintained over the full range of blend ratios. The substitution of dimethyl rubber for a portion of FSR sacrifices some of the gasoline resistance of the FSR. Despite an increased swell of these FSR/VMQ blends in the presence of an aggressive solvent such as gasoline, the resistance to oil is outstanding and far superior to that of dimethyl rubber by itself.

The volume swell is directly related to the percentage of FSR. Volume swell is done on uncompressed samples. Compression can positively influence the VMQ phase[1].

Achieving Lower Cost Using EXACT Performance Compounds

Combining FSR with extending fillers can be done either during the manufacture of a base by combining two bases, or during compounding. In either case, it takes significant expertise to ensure excellent dispersion of the two materials into one another.

Once that is done, it is possible to adjust the performance of the FSR to create a material within the desired target swell in fuel and oil. In addition to reducing the overall cost in end use, an excellent side effect of the addition of filler is reduction in swell, which is particularly evident when exposed to Ref. Fuel C, as shown by the red line in Figure 5.

Here the combination of 60 parts per hundred filler and 20 weight percent VMQ in the formulation maintains a swell of about 35% in Ref. Fuel C at an attractive price per liter of the material (see Figure 8).

Moreover, because both polymers are silicone-based, there is no compromise in the range of temperature at which these materials will perform effectively and consistently.

Figure 7: Comparison of typical properties between cost-effective filled FSR, FSR and other high-performance elastomers

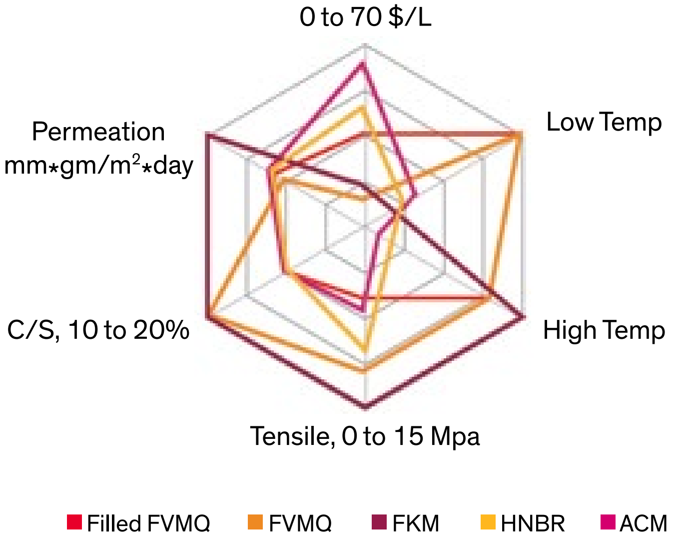
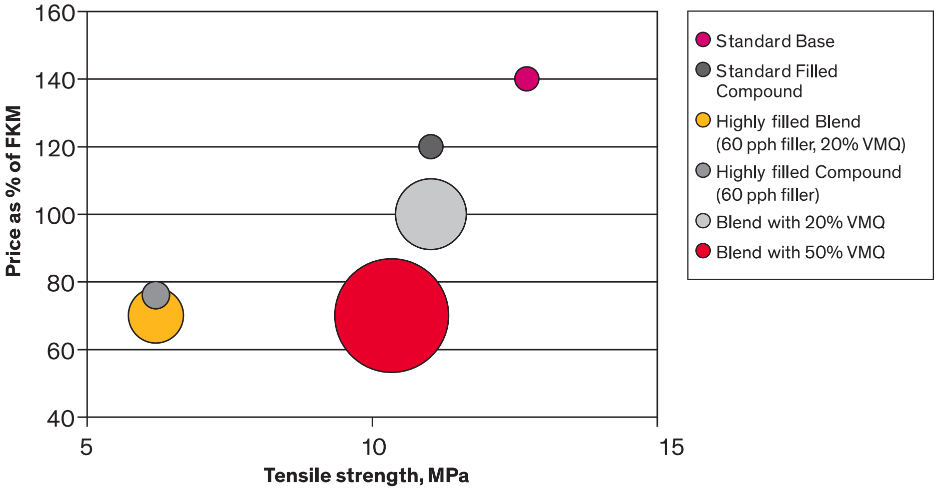


Figure 8: Oil swell, strength and cost



Overall Performance Comparisons

Using particulate filler to reduce swell and end costs does not reduce chemical, fuel and solvent resistance. In fact, they may even be enhanced by the presence of the particulate filler. These extended blends of VMQ, filler and FSR rubber can be used to prevent weep and reduce hydrocarbon permeation in engine-oil-sealing gaskets while exhibiting excellent low-temperature performance.

Price-performance Comparisons

In applications that can accept the use of lower tensile strength and stiffer elastomers, these FSRs can be extremely cost-effective. Many rubber applications require good compressive strength, for which these compounds would be ideally suited. When the comparison is made between other high-performance elastomers and a properly compounded FSR, it is clear that, in many instances, FSR is now the more cost-effective material.

In this price-performance example (Figure 8), the vertical axis represents a price per liter comparison of various FSR compounds with a standard 66% fluorine-containing FKM copolymer. The horizontal axis is tensile strength in MPa. The diameter of the circle represents the degree of swelling of the uncompressed rubber. This gives an idea of the price-performance range versus the oil swell and illustrates the broad range of possibilities available for part designers and engineers. This price comparison is for illustrative purposes only, and actual pricing may be different depending on the application and volume.

Design Opportunities for Engineers

The SILASTIC™ FSR product range from Dow includes a wide range of solutions, consisting of liquid FSRs, different types of gums and dozens of high consistency bases. From these high-performance elastomers, Dow formulates custom compounds to meet your needs.

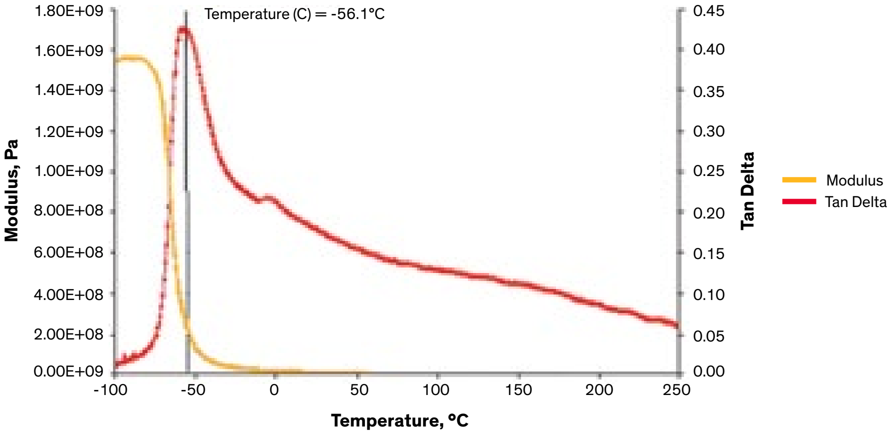
This extensive product range means competitive solutions for manufacturers of seals, diaphragms and other high-performance rubber parts.

- Fuel line quick-connect seals
- Electrical connector inserts
- Air pump valves
- Exhaust gas recirculating diaphragms
- Fuel-resistant hydraulic and electrical clamp blocks
- Vapor recovery management system seals
- Natural vacuum leak detection control diaphragms
- Engine gaskets
- Fuel line pulsator seals

The different gums enable custom bases, to be created and tailored to meet exact performance profiles. From those bases, there is literally an infinite number of different compounds that can be designed and manufactured, each one tailored to meet exactly the performance and cost targets of the application.

This almost infinite number of FSR compounds can be classified into two product forms: a high consistency rubber form and a liquid silicone rubber form (LSR). These liquid forms allow rapid processing in unattended injection molding machines. It is as simple as loading the machine with part A and part B, switching it on, and walking away. These are the promises of using fluoro LSRs: significant labor cost savings and more consistent product quality.

Figure 9: Dynamic mechanical properties of the test compound based on SILASTIC™ LS 5-2060 Fluorosilicone Rubber



The applications for FSRs are virtually unlimited:

- Where fluid resistance is needed
- Where consistent mechanical properties are needed
- And in high and low temperatures

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[1] Brumels, Mark D.; Olsen, Jr., Charles W.; Irish, Paul T.; and Altum, Stephen C. “The Effect of Compression on Permeation of Hydocarbons through Dimethyl and Flourosilicone Rubber” SEA 2003-01-0945

Figure 10: Dynamic mechanical properties of the test compound based on SILASTIC™ LS-2860 Fluorosilicone Rubber

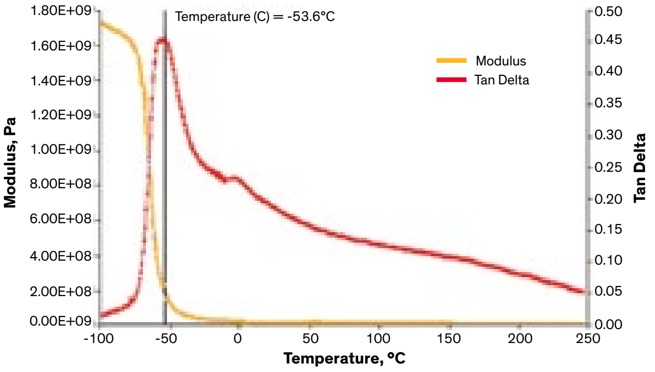


Figure 11: Dynamic mechanical properties of the test compound (37V) based on 66% fluorine dipolymer

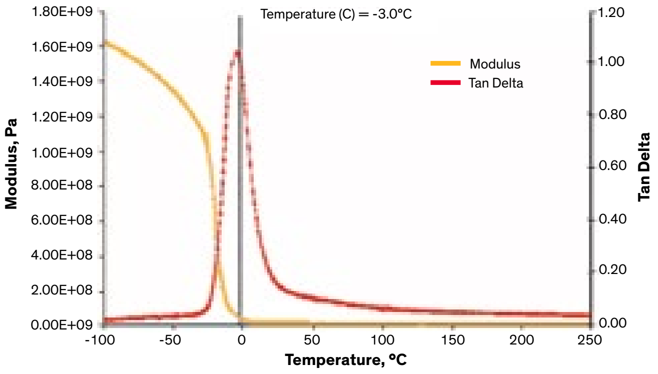


Figure 12: Dynamic mechanical properties of the test compound (38V) based on 68% fluorine terpolymers

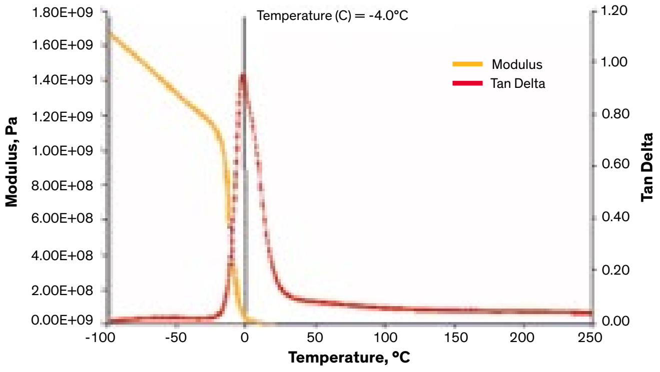
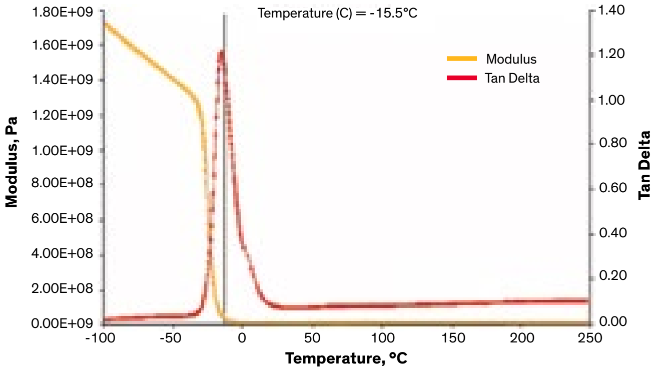


Figure 13: Dynamic mechanical properties of the test compound (39V) based on 67% fluorine terpolymer manufactured utilizing the latest technology



Conclusion

Through Dow's legacy of technology expertise and continuing innovation, it is now possible to obtain tailored compounds to meet the needs of your company. Compounding to your exact mechanical, handling and price targets enables customers to be competitive in a cost-sensitive environment. Dow's application engineers and scientists work closely with customers to develop elastomer solutions to exactly meet their needs.

Continuous improvement of Dow's FSR elastomer technology has resulted in rubber materials that can exhibit abrasion resistance superior to FKM while exhibiting very low swell in typical lubricating oils. These materials open the possibility for the use of FSRs in dynamic applications that require excellent performance at temperatures beyond the range of conventional fluoroelastomers.

Addendum

The previous DMA curves were generated during the Rapra Technologies comparative testing of the FSR and FKM compounds.

Dow Brands Serve You

Whether you seek industry-leading innovation or greater cost efficiency, Dow can help. DOWSIL™ and SILASTIC™ solutions deliver specialty materials, collaborative problem-solving and innovation support tailored to your needs. See details at **consumer.dow.com/auto.**

To learn more about how our engineered elastomers can help meet challenging design needs in automotive and transportation applications, contact your Dow Technical Representative or visit **consumer.dow.com/ContactUs**.
