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Closing the Fluoro Elastomers High Temperature Gap: New Developments in Fluorosilicone Rubber

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Abstract

As rubber applications continue to evolve and require higher-temperature performance and higher resistance against fuels and oils, many industries – including automotive, aviation, and oil and gas – are looking beyond traditional materials for solutions. Applications include everything from turbocharger hose lining to blowback preventer seals to gaskets for airplane hydraulic systems. FKM (fluorocarbon rubber) and FVMQ (fluorosilicone rubber) have historically been used in these applications, with FKM being used for many of the applications requiring the highest-temperature resistance and FVMQ being used for temperatures up to 220°C. Recent advancements in FVMQ technology have extended the upper service-temperature performance up to 240°C with peak temperatures to 250°C.

This advancement, in addition to greater property stability over a wide temperature range compared to FKM, now allows FVMQ to be used in higher-temperature applications. Additionally, FVMQ provides 25% lower density, allowing for better weight savings and lower material usage. This paper discusses the technology advancements in FVMQ, showing comparisons to traditional FVMQ and FKM materials. Comparisons will be made to newly developed FVMQ materials with higher heat stability, showing test results for physical properties measured at elevated temperature (up to 200°C), aging performance in automotive fluids (fuels and oils), adhesion performance to VMQ (as it relates to co-extrusion application), and acid-gas resistance. This paper will demonstrate how FVMQ elastomers can be designed to precisely meet specific application requirements and highlight performance attributes in which FVMQ provides advantages over FKM.

Introduction

To keep pace with change in the automotive industry, manufacturers are facing a number of pressures. There are regulatory and governmental mandates and continuous cost-reduction initiatives. In addition, new customer preferences are shaping design trends for smarter, safer and more energy-efficient vehicle technologies, along with steadily reducing environmental impact.

Intending to meet these needs, many initiatives – such as weight reduction, use of smaller yet more powerful engines, and increased electronics content – have created additional challenges for suppliers and manufacturers. Megatrends in vehicle design requirements present many significant technical challenges for fuel economy improvements, emissions reduction, vehicle control and occupant comfort.

To match the advancements in vehicle design and systems technology, traditional materials are being pushed to deliver performance aspects that extend beyond the requirements they were originally developed to meet.

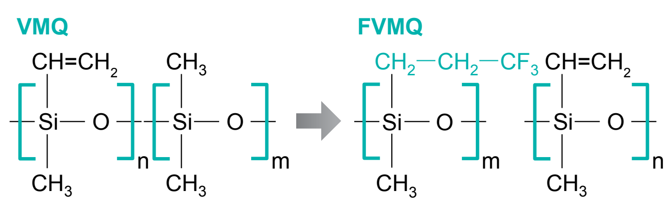
Fluorosilicone elastomers are one class of traditional materials being expected to deliver innovative solutions to enable these new technology advancements. The use of alternative fuels, synthetic oils and aggressive fluids; increased operating temperatures with less cooling airflow; lighter-weight vehicles with reduced material consumption; and global vehicle platforms all pose unique challenges related to material performance. First developed in the 1950s to provide high resistance to fuels, oils and solvents in applications across a broad temperature range, fluorosilicone rubber (FVMQ) development has continued to evolve and, as a result, has found wide use in automotive, aviation and industrial applications for many decades now.

Close collaboration with these industries and/or markets is necessary to ensure technology development of fluorosilicone rubber results in innovations that can help customers meet design trends for performance improvement and cost reduction. This paper highlights some key advancements in fluorosilicone rubber, developed in response to industry expectations for improved materials to meet challenging automotive-design trends.

Basic Fluorosilicone Technology

Fluorosilicone rubber is formulated from fluorosilicone polymers that contain a (-Si-O-) repeating group on the polymer backbone. One unique difference, compared to their dimethylsiloxane counterparts, is the incorporation of a fluorine component attached to the polymer backbone. Fluorosilicone polymers replace one (methyl) side group on each silicon with a (trifluoropropyl) side group (Figure 1). The resulting polymer retains dimethylsilicone's durability in very hot and very cold temperatures while adding high resistance to nonpolar solvents and aggressive fluids. A vinyl side group also can be added to allow the polymer to be crosslinked. These polymers are then utilized to produce fluorosilicone rubber, which is commonly referred to as FVMQ (fluorovinylmethylsiloxane) per ASTM 1418. Depending on the application, FVMQ technologies compete directly and indirectly with carbon-based fluoroelastomers such as fluorocarbon rubber (FKM).

Figure 1.
Structure of silicone and fluorosilicone rubber



Early applications for fluorosilicone rubber technology involved various aerospace vehicles and equipment as well as a number of military aircraft programs, most commonly for seals exposed to fuels and hydraulic fluids. Automotive applications include a wide range of fuel-resistant sealing and gasketing applications, as well as membranes, diaphragms and flexible valves for fuel and vapor recovery systems. Fluorosilicone rubber is especially beneficial for chemical-resistant liners on turbocharger hoses exposed to temperatures exceeding 180°C and is commonly used in combination with an outer layer of reinforced HCR (high-consistency rubber) dimethylsilicone elastomer. FVMQ-HCR hoses have broad application in light-duty and heavy-duty trucks. In addition, fluorosilicone rubber has found wide use in applications requiring high chemical resistance when exposed to low temperatures or when a soft material with high chemical resistance is required for sealing applications. Unlike many fluorocarbon elastomers, fluorosilicone rubber can be used in applications requiring temperature exposure down to -65°C in addition to applications requiring low modulus and hardness values below 40 Shore A durometer.

Silicones are known as an enabling technology with unique properties not offered by other materials. The versatility of silicone chemistry helps to create numerous opportunities for developing specialized fluorosilicone rubber bases and custom compounds to meet specific application needs – exactly what today's design trends demand.

Innovation in FVMQ

A multigenerational approach to improvement of FVMQ technology has been used that is focused on market needs for higher-temperature resistance and improved thermal stability, increased fuel resistance, and higher adhesion to VMQ. These market needs, in conjunction with close collaboration with end users, has enabled the development of specific, fully formulated compounds designed to meet critical customer requirements and provides an expanded FVMQ toolbox of new technologies that can be applied to many other industries and applications. Use of a platform project that explores all aspects of FVMQ technology – including new additives and intermediates; improvements in thermal stability; higher adhesion to VMQ; and improvements in compression set, handling, and fuel and oil stability – expands the use of FVMQ in applications where the material may not have been considered in the past.

Activities in this multigenerational project plan are continually evolving to find and resolve gaps between current technology and new market and customer needs requiring improved performance of FVMQ solutions. This has led directly to the commercialization of new compounds available to the market that address many of these performance gaps, such as higher-temperature performance for turbocharger hoses (TCH) and other applications, low compression set for better sealing, and higher fuel resistance and retention of properties after immersion.

High-Resilience and Low-Compression-Set Developments

New FVMQ bases have been developed to meet needs for high resilience/rebound, low compression set, low volume swell in fuel, reduced stickiness when unwrapping and mill handling, and improved ply adhesion when cured with VMQ.

Specially formulated to meet fabricator, compounder and specifier needs, two uncatalyzed FVMQ materials were developed with a choice of either 40 or 70 Shore A durometer cured hardness. These fluorosilicone rubbers are designed to help optimize sealing performance and to provide both easy processing and process versatility. Both FVMQs offer extremely low compression set, which is a critical property required to improve long-term durability for components like O-rings and seals. These materials achieve compression set values below 10% when post-cured and tested at 175°C for 22 hours, as well as comparatively low compression set at the harsher conditions of 70 hours at 200°C. These unique FVMQ products also offer high resilience for dynamic sealing applications and stable performance properties, even with no post-curing.

These new FVMQ materials provide typical fluorosilicone rubber properties – including excellent resistance to fuels, oils, solvents and aggressive fluids – with low volume swell. In testing, the fluorosilcone rubber materials each exhibit excellent fluid resistance with low volume swell when exposed to a variety of different fuels and oils. In addition, good property retention and aging resistance are seen over a wide service-temperature range. These performance attributes can be further enhanced for specific needs.

In terms of better handling characteristics, these specialty FVMQ products can be custom-compounded, pigmented, blended, modified with additives and easily processed. With custom compounding, specific performance attributes can be especially tailored for particular application requirements, including increased temperature resistance. Pigment masterbatches provide easy coloring, while performance additives are available for addressing a variety of other needs. In addition, the new products can be blended with each other to achieve intermediate hardness levels, or they can be blended with other fluorosilicone or silicone bases for further tailoring of uncured and cured properties.

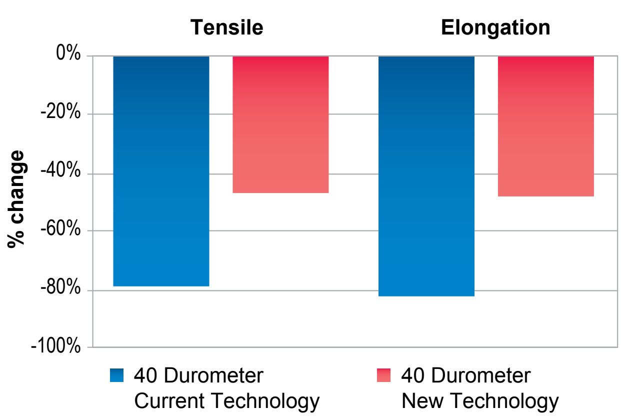
These materials are designed for molding, extrusion and calendering processes and for applications such as O-rings, diaphragms and other fuel contact applications. The improved adhesion of these products to VMQ allows this technology to be used for TCH applications where adhesion to VMQ is necessary for reliable performance.

FVMQ for Higher Operating Temperatures

Development efforts focused on a more heat-resistant FVMQ technology for extreme high-temperature applications aim to meet more stringent component-design and reliability requirements demanded for under-the-hood applications. These performance and reliability requirements are necessary due to much higher operating temperatures seen with smaller and more powerful engines, increased exhaust gas recirculation, advanced emission controls, and more underhood content with less airflow.

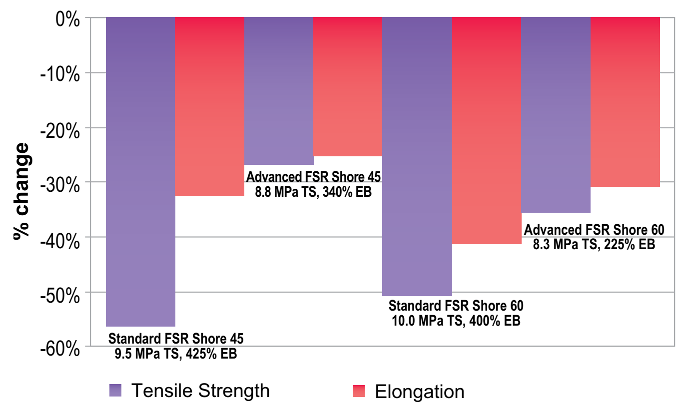
In close collaboration with specific customers and end users, a diverse, global team of scientists and engineers responded to specifications calling for increased heat-resistance properties in fluorosilicone rubber. With specific milestones and targeted improvements in the development process, the team worked closely with fabricators and specifiers to develop the custom FVMQ technology and to validate its performance with high-temperature aging tests (Figure 2).

Figure 2.
Heat aging 14 days at 250°C



Previously limited to applications with long-term exposure to application temperatures of 200°C or less, fluorosilicone rubber can now be custom-compounded for automotive components that must withstand continuous temperatures up to 220°C and limited-time peak temperatures up to 240°C or beyond. Rigorous heat-aging tests show considerable improvements in retention of tensile strength and elongation, as well as improved performance when exposed to aggressive fluids in extreme heat (Figure 3).

Figure 3.
Property change after immersion in automatic transmission fluid for 168 hours at 150°C



FVMQ Stability

Several degradation mechanisms were researched and investigated to better understand FVMQ thermal stability. These degradation mechanisms occur at different temperatures and rates and under different environmental conditions. Therefore, different technology solutions are required to address all of these failure modes with minimum negative impact on other properties.

Degradation mechanisms of FVMQ include chain cleavage and depolymerization, oxidative cleavage of crosslinks and side groups, and changes to filler/polymer interactions.

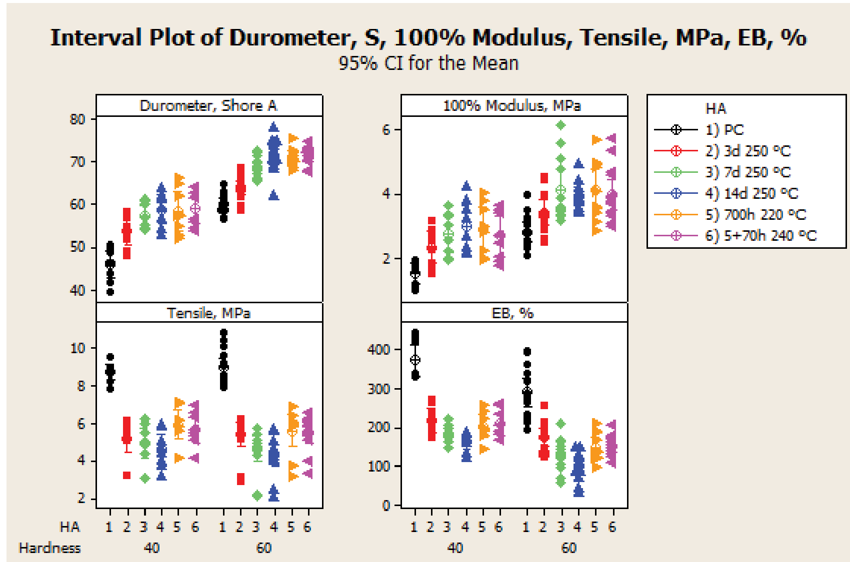
These materials were tested in a range of environments, including:

- Dry heat
  - 70 hours to 14 days at 250 to 275°C
  - 700 hours at 220°C plus 70 hours at 240°C
- Oil – Dexron® VI used as an aggressive test oil, 7 days at 150°C
- Compression set – 3 and 7 days at 200°C
- Fuel
- Acid gas condensate

Analysis of Heat Age Conditions

A comprehensive approach was executed to understand the impact of various exposure times and temperatures on FVMQ degradation. The data generated from this comprehensive evaluation identified accelerated higher-temperature aging conditions comparable to longer-term lower-temperature conditions typically required for specifications (Figure 4). Identifying short-term testing conditions was critical for accelerating development activities and providing quicker results while still allowing long-term aging performance to be predictable. In addition, performance at a given condition can vary widely by the FVMQ sample, which allows a better understanding of technology changes and their impact on performance at various conditions.

Figure 4.
Interval plot of heat aging



Properties at Temperature

Though FVMQ has lower tensile strength than FKM at room temperature, property performance at elevated temperatures is similar between FKM and FVMQ when evaluating tensile strength and is higher for FVMQ when evaluating elongation at break. FVMQ materials are stable over a wider range of temperatures than FKM and can have higher performance at elevated temperature. Material properties at elevated temperature often are not considered even though the application may be exposed to these elevated temperatures. (Figures 5, 6 and 7).

Figure 5.
Tensile strength of FVMQ and FKM at various temperatures
Dumbbells placed in grips and measured ~15 when oven is at temp

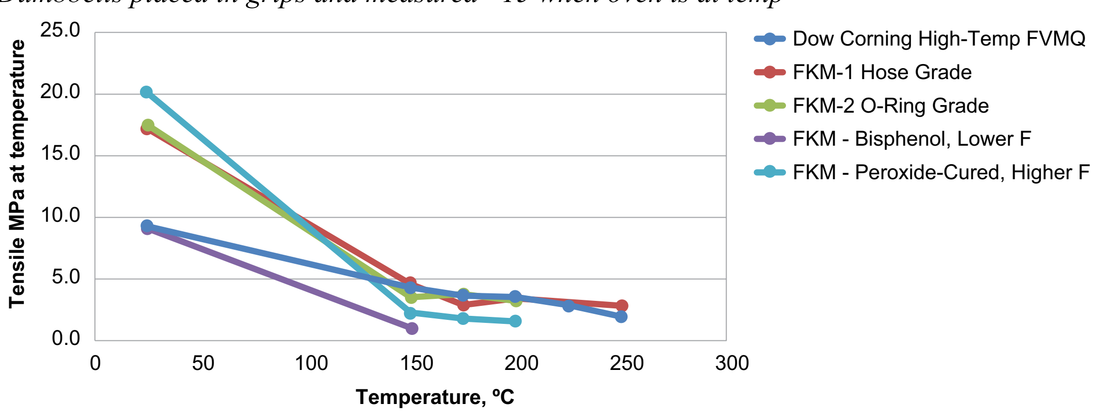


Figure 6.
Elongation of FVMQ and FKM at various temperatures
Dumbbells placed in grips and measured ~15 min after oven is at temp

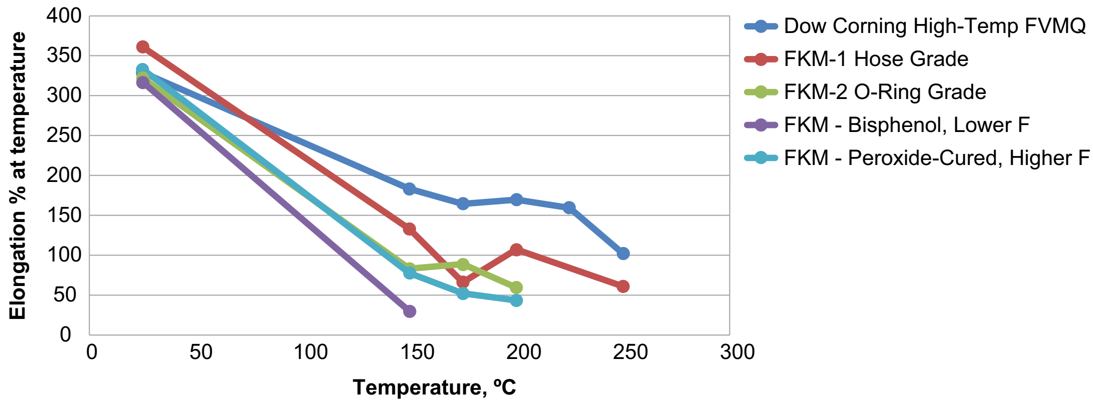
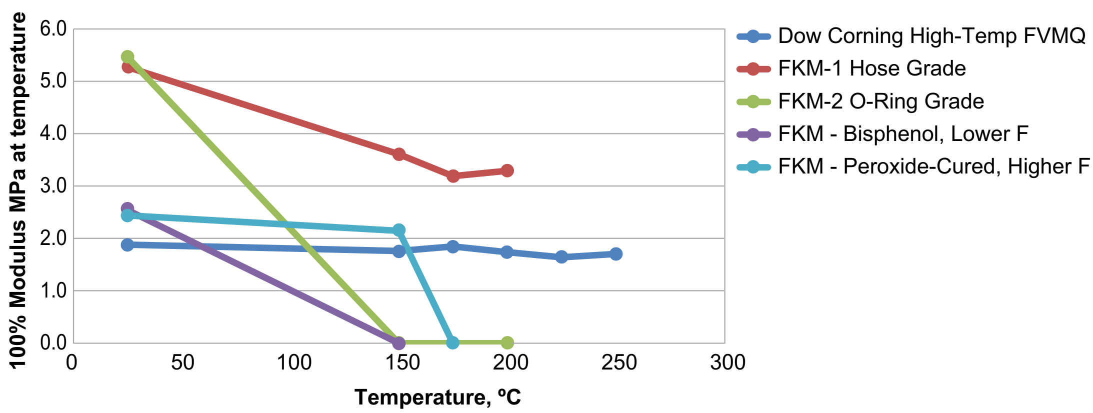


Figure 7.
Modulus of FVMQ and FKM at various temperatures
Dumbbells placed in grips and measured ~15 min after oven is at temp



Conclusion

With in-depth industry experience, materials creativity and problem-solving collaboration, teams of leading scientists and application engineers are succeeding in generating significant upgrades in fluorosilicone rubber capabilities. This proven, effective solution for durable automotive components exposed to aggressive fluids and very hot or cold conditions can now be custom-compounded for better handling characteristics, as well as for extremely high continuous and peak temperatures. In addition, improvements in compression set, resilience and acid-gas resistance also have been achieved, which allows OEMs, specifiers and end users another material option to consider for challenging applications requiring these improvements. These technology upgrades can be built into the full range of fluorosilicone rubber choices and tailored to meet customers' precise application requirements.

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