Advances in Fluorosilicone Compounds for Turbocharger Hose Liners and other Transportation Applications

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Abstract

Turbocharger hose use has undergone significant growth in recent years. In the US, turbocharged engines are increasing in heavy duty pick-ups, and have been in common use for large (e.g. Class 8) tractor trailer vehicles. In Europe, the growth of turbodiesel engines for passenger cars has resulted in increasing demands of the materials used in these system components.

Flexible hose sections are being challenged to perform in harsh environments. Increasing temperatures and pressures are required in service. Barrier properties of hot exhaust containing aggressive petrochemicals and other combustion by-products are necessary.

The typical construction for turbocharger hoses utilizes VMQ silicone with a fluoroelastomer liner (FVMQ fluorosilicone or FKM fluorocarbon). To contain the pressure and vibration at temperature, multiple layers of a high temperature fabric (e.g. aramid) are part of the overall, reinforced hose assembly.

Significant progress has been made to address the increasing demands on fluorosilicone rubber compounds used in turbocharger hoses. Aggressive hot oil resistance, higher service temperatures, compound economies, and improved adhesion to VMQ silicone are some of the areas that will be presented.

The development and data presented is centered on turbocharger hose and similar under hood applications. These findings, however, can be used as technical enablers for a wider understanding of the flexibility and performance of fluorosilicone use for other oil, solvent, and fuel resistant opportunities.

In addition to the presenter, significant contributions to this paper include Dave Lawson, Rob Drake, Steve Robson, Steve James, Bruno Cuocci, and Fabio Giambelli.
INTRODUCTION

The use of turbochargers has been growing in the US and Europe. Over recent years the passenger car market in Western Europe has enthusiastically embraced turbo diesel engine technology. Modern diesel engines have been able to achieve significant advancements in terms of increased power, noise reduction, fuel economy and the all-round driving experience. In many Western European countries they now outsell their gasoline engined equivalents.

In the US, the recent growth has been (primarily) in the large ‘pick-up’ truck segment. The “Big 3” automobile manufacturers are the main players and specifiers for this segment. Historically, turbocharged diesel engines have been in common use for large (Class 8) heavy duty trucks. These truck manufacturers include common names like Freightliner, Navistar, Peterbilt, Kenworth, Volvo Trucks, Mack, Sterling, and Western Star. The three main engine manufacturers for these OEMs include Caterpillar, Cummins, and Detroit Diesel.

A flow diagram of a typical turbo diesel engine is shown in Figure 1.

In addition to the turbocharger, most systems utilize an air-to-air heat exchanger commonly known as a Charge Air Cooler (CAC) or Intercooler. In these trucks, a total of six hoses are used. A continuous operating temperature requirement of the hoses of greater than 175°C is typical.

Turbocharger design has also changed beyond recognition, with increasing demands being placed upon the materials of construction. Hose sections in particular have been challenged to adapt to rising temperatures and more aggressive engine oils. Many hoses that previously used acrylic rubbers such as AEM have transitioned to silicone rubber in order to maintain their flexibility at increasingly elevated temperatures. However, in general this has also necessitated the incorporation of an additional liner of fluoro-elastomer to provide the desired level of oil resistance. Figure 2 shows a typical construction.

In most cases, aramid fiber fabrics are used in hose construction. The aramid fabric provides the hose’s underlying strength, while the silicone rubber serves to protect the fabric and give the finished hose its flexibility and resistance to extremes of temperature. In the case of Silicone rubber for turbocharger hose applications, we use a 1-part High Consistency Rubber (commonly abbreviated as HCR). The rubber is normally calendered onto the fabric to prepare the material for hose construction. Due to the continuous use temperatures in excess of 170°C, it is generally necessary to employ silicone rubber (VMQ) in both the middle and outer layers.

When specifying the fluoroelastomer liner, fabricators and/or end users will have to choose either Fluorosilicone rubber (FVMQ) or Fluorocarbon (FKM).
The hose liner is in direct contact with exhaust gasses and therefore has additional service requirements. Typical performance requirements for this inner layer would include the following criteria:

1. Temperature resistance
2. Oil resistance
3. Fuel resistance
4. Interlayer adhesion
5. Processing characteristics (calender and/or co-extrusion)

Technical personnel at Dow Corning have worked to develop solutions to address these new, tougher performance requirements. Data from standard, commercially available Dow Corning Fluorosilicone bases are compared to experimental formulations. Each of these criteria will be examined with supporting test data.

TEMPERATURE RESISTANCE

There has been an increase in overall performance of modern diesel engines which has translated to a trend towards higher temperatures under the hood. In the passenger car segment, as diesel engines have proliferated in Europe, they have inevitably cascaded down from luxury models into many small and medium sized cars, with limited space under the hood for heat dissipation. It’s quite common therefore to see continuous use temperatures of > 200°C; necessitating the replacement of organic rubbers and thermoplastics by silicone rubber.

The fluoroelastomer liner will experience similar temperatures to the HCR layers; hence a similar level of heat resistance is required. Typical specifications call for good retention of physical properties after continuous exposure to the target temperature. A common requirement would be to survive 7 days heat ageing @ 200°C with minimal change in durometer, tensile strength, and elongation at break. Typical results for a range of FVMQ materials are shown in Figure 3.

The data shows that many of our commercially available FSR materials already exhibit reasonable stability to this heat ageing regime (loss in tensile strength of 15-20% and loss in elongation of 5-10%). Several experimental formulations are also shown, whereby materials have been formulated that produce minimal change in BOTH tensile strength and elongation (typically around 5% property change in both cases).

Recognizing that the target hose may well experience significant temperature excursions above 200°C, we have also generated a dataset based on exposure to 7 days @ 225°C. Selected results are shown in Figure 4.

Figure 3

Figure 4.
The increased severity at a 25°C higher test temperature is immediately apparent. Commercial materials now show a wide range of property changes, with tensile strength loss anywhere between 40 and 80%. Again, however, we have several experimental candidates that restrict this loss to 25-30% while also showing minimal change in elongation at break. This data clearly suggests that the materials will retain excellent elastomeric properties even under these extreme conditions of heat exposure.

Many standard tests involve heat ageing of the material and subsequent measurement of physical properties. Typically these properties are determined AFTER the material has equilibrated back to ambient temperature. While this approach gives one view of the material’s high temperature stability, this bears little resemblance to potential failure modes during service. In the real world we might expect a part to fail while at its service temperature, not when it has cooled back down to room temperature conditions. The following tables (Figure 5 – 8) represent data from a series of products tested at an independent rubber test facility (Rapra Technologies). Two FKM compounds and two FVMQ compounds are compared at ambient and elevated temperatures.
OIL RESISTANCE

One key requirement in this application is for the turbocharger hose liner to survive extended contact with hot engine oils. At a basic level, the liner must act as a barrier layer and prevent oil from weeping into the medium and outer layers of the hose. Beyond this primary requirement, further testing is usually based on a total immersion method at oil temperatures of 150°C, 175°C, and 200°C (or even higher). Modern engine oils themselves have trended towards fully synthetic grades with additive packages that yield excellent anticorrosion properties and extended service intervals (these additives include materials such as zinc alkyl dithiophosphate, alkyl or aryl modified amines and alkyl phenols). Commonly specified oils for this application would include the following:

- Total MA3 5w30
- Cecilia 20
- Shell Helix Plus 10w40
- Castrol SLX Longlife 0w30.

Most of our recent testing has focused on Total MA3, in view of its reputation as a highly aggressive test oil and its widespread use in Europe as factory fill oil for both diesel and gasoline engines.

Initial testing with Total MA3 @ 175°C certainly confirmed the aggressive nature of these test conditions. Clearly both the oil type and the temperature are playing a part in the dramatic degradation that occurs (specifications for the other common test oils often require immersion @ 150°C). Rates of rubber degradation are dramatically increased as temperature is ramped up from 150 to 175°C.

Further investigation, however, has highlighted some very significant differences that can be related back to the FSR formulations and structures. While our initial experiments gave tensile strength loss of as much as 80% we now have many candidate formulations that have reduced this property change to between 10 and 30%. Figure 9 shows some selected data arranged in order of % loss in tensile strength.

At first sight many of our conclusions appeared contrary to traditional logic. Conceptually we had postulated that a high strength FVMQ would be most appropriate for such a demanding application. However, we have generally seen the opposite effect whereby these stronger materials are more susceptible to degradation in oil. For example FVMQ such as LS5-2040 with initial tensile strength of 12 MPa is quite often degraded to about 3 MPa after the relevant exposure to MA3, i.e. a loss of around 75% after 7 days immersion @ 175°C. Conversely, our most successful FVMQ grades are those with a starting tensile strength of 9-10 MPa. Test data indicates that these will typically retain the majority of their initial strength after the same oil exposure. See especially the results for FSR materials LS5-8740, LS-2380 and LS4-9038 in Figure 9.

![Figure 9](attachment:Figure9.png)
**FUEL RESISTANCE**

Resistance to gasoline fuel is required, although to a much lesser degree than oil in this application. Specifications typically call for a Fuel C immersion test and we can obtain satisfactory results with a variety of fluorosilicone rubber formulations.

Volume swell is perhaps the most relevant parameter, with values of < 25% being acceptable (and easily achievable) after 7 days immersion at ambient temperature (usually specified as 23°C).

**INTERLAYER ADHESION**

Along with satisfactory oil resistance, adhesion represents the other critical parameter for successful adoption of a fluoroelastomer hose liner. Integrity of the finished hose depends upon not only an acceptable initial bond strength, but also upon its ability to survive the influences of temperature, oil and the effects of pulsation/vibration experienced during service.

Representative adhesion testing involves joining together uncured sheets of the appropriate HCR and FSR layers. This composite is then press cured under moderate pressure only and cut into strips for peel testing to quantify the bond strength between the two materials. Usually a small piece of plastic film is used to hold an initial section apart and hence allow the two ends to be clamped in the jaws of the tensometer. Figure 10 illustrates how the sample is prepared. Figure 11 shows some of the early results of recent laboratory developments.

Unmodified materials will frequently yield a peel strength of 1 N/mm or less. In some cases this may be acceptable, but quite often this type of result translates to borderline adhesion in a finished hose. However, via a comprehensive screen of additives we have been able to demonstrate up to a 3-fold improvement over this baseline bond strength. Formulations 1 and 2 in Figure 11 are typical of the results we can now achieve.

**PROCESSING CHARACTERISTICS**

Many of this application’s more intangible requirements can be captured within this category. Here we can consider properties of a liner that make it suitable for calendering and/or co-extrusion techniques (hardness, green strength, etc.). In addition, features such as cure speed and the cure process (steam or hot air; pressure or open oven) are some of the variables that must be taken into consideration when optimizing a compound.

Fluorosilicone rubber is available in a wide range of properties, and is suitable for applications involving both calendering and extrusion. Durometer can range from as low as 20 up to 80 Shore A. This allows a huge degree of flexibility in matching a material to the processing characteristics required. Correct formulation can provide the appropriate level of green strength in order to minimize hose sag in an extrusion based process.
One key advantage of the HCR:FSR combination is our ability to closely match the cure speed of both layers. We believe this to be an important factor with respect to interlayer adhesion, whereby this adhesion has the chance to develop fully during the co-curing process. In the event of mismatched cure speeds, adhesion must develop while one layer has at least a partial cure. This reduces the potential for intimate contact and interpenetration of the two materials. We also believe that our ability to closely match the durometer of both HCR and FSR is again a contributory factor in this interpenetration of the two material layers.

Of course the ultimate test is that provided by hose fabrication trials. It is here that we are able to challenge and/or validate the laboratory findings and related theories that have developed. In this respect we rely on healthy technical exchange and relationship building with expert fabricators in this field.

IMPROVING COMPOUND ECONOMIES

There are four general areas that can improve the economies of using fluorosilicone for various applications. These include:

1. Blends with VMQ silicone
2. Use of high filler loading
3. Addition cure technology
4. Fluorosilicone Liquid Silicone Rubber (FLSR)

BLENDS
In some applications, the resistance to aggressive hot oils (and oil vapor) would normally lead one to utilize a fluorosilicone solution. The common resistance to this choice is usually cost. Now more than ever, we as formulators must be diligent with identifying the job to be done and keeping an open mind to solution development. Blends of FVMQ and VMQ may offer an acceptable level of intermediate fluid resistance while improving processing characteristics and product economics. The use of VMQ as a diluent in an FVMQ formula can help to maximize the value of parts fabrication. In most cases, by using VMQ as a lesser ingredient, the specific gravity decreases compared to 100% fluorosilicone and the mechanical, physical properties can be maintained. In all blends, however, the volume swell in aromatic oils, fuels, and some solvents is directly related to the FVMQ content.

FILLERS
Although the use of filler to improve compound economics (thereby maximizing value) may be obvious, the newer, high strength fluorosilicone bases can offer the formulator the option to incorporate high filler loadings while maintaining respectable properties. Figure 12 represents data of two fluorosilicone formulas at low and high filler loadings tested to a typical ASTM line call out for fluorosilicone materials (ASTM D2000 M2FK606 A19 EA36 EF31). For the test specimens, slabs were press cured for 10 minutes @ 177°C, and oven post cured for 4 hours @ 200°C.
<table>
<thead>
<tr>
<th>Original Properties</th>
<th>ASTM limits</th>
<th>50 Duro low filler</th>
<th>55 Duro high filler</th>
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<tr>
<td>Specific Gravity</td>
<td>None</td>
<td>1.493</td>
<td>1.704</td>
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<tr>
<td>Durometer, Shore A, pts</td>
<td>55 – 65</td>
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<td>Tensile Strength, MPa</td>
<td>≥ 6.0</td>
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<tr>
<td>Elongation at Break, %</td>
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<td>259</td>
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<tr>
<td>Modulus @ 100%, MPa</td>
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<td>2.2</td>
<td>3.4</td>
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<tr>
<td>Tear Strength, Die B, kN/M</td>
<td>None</td>
<td>20.7</td>
<td>19.8</td>
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<tr>
<td>Compression Set, plied disks</td>
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<td>22 hours @ 175°C, % set</td>
<td>Basic Req’ts</td>
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<td></td>
</tr>
<tr>
<td>Volume Change, %</td>
<td>≤ 50</td>
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<td>15.7</td>
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<tr>
<td>IRM903 Oil Age 70 hours @ 150°C</td>
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<td></td>
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<tr>
<td>Volume Change, %</td>
<td>≤ +10</td>
<td>+4.3</td>
<td>+5.0</td>
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<tr>
<td>Heat Age 70 hours @ 200°C</td>
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<td></td>
</tr>
<tr>
<td>Durometer change, pts</td>
<td>± 15</td>
<td>+7.1</td>
<td>+0.5</td>
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<tr>
<td>Tensile change, %</td>
<td>± 30</td>
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<td>-11.0</td>
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<tr>
<td>Elongation change, %</td>
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<td>-30.1</td>
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<td>Heat Age 70 hours @ 225°C</td>
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<td>A19 Req’ts</td>
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<td>+9.7</td>
<td>+1.3</td>
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<tr>
<td>Tensile change, %</td>
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<tr>
<td>Elongation change, %</td>
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</tr>
<tr>
<td>IRM903 Oil Age 70 hours @ 150°C</td>
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<td>EA36 Req’ts</td>
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<tr>
<td>Durometer change, pts</td>
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<tr>
<td>Tensile change, %</td>
<td>- 35 max.</td>
<td>-14.9</td>
<td>-20.6</td>
</tr>
<tr>
<td>Elongation change, %</td>
<td>- 30 max.</td>
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<td>Volume Change, %</td>
<td>0 to +10</td>
<td>+4.3</td>
<td>+5.0</td>
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<tr>
<td>Fuel C Age 70 hours @ 23°C</td>
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<td>EF31 Req’ts</td>
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<td>-19.2</td>
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<td>-24.3</td>
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<td>Volume Change, %</td>
<td>0 to +25</td>
<td>+17.8</td>
<td>+17.3</td>
</tr>
</tbody>
</table>

Figure 12.
ADDITION CURE TECHNOLOGY

Platinum or addition cure technology is not new. In VMQ materials, platinum cure HCR and LSR offer high speed cure and process ease. With fluorosilicone, the higher mold speed by itself is not enough to justify the switch. When we listened to our customers, there were a number of commonalities that we heard concerning the processing problems that they had when they molded parts made from fluorosilicone. Some of the common issues were:

- Sticky flash causing cured in/cured on flash
- Sticky flash causing stuck on flash
- Slow cure times
- Slow cryogenic deflash rates, and high levels of coolant required
- Slow inspection rates

By utilizing platinum cure technology for fluorosilicone, we were able to address most of the processing issues. Through plant trials at our customers, we were able to document some of the true process advantages of platinum cured fluorosilicone.

- Faster cure rates
- Cleaner running molds
- Not Oxygen Inhibited
- Dry, fully cured flash and less tacky parts
- Quicker deflash cycles
- Improved inspection rates

It was determined that real process benefits are achievable. Critical to understanding the value of this benefit is understanding the activity based costing of the process. By using addition cure technology in fluorosilicone, process derived scrap can be significantly reduced.

LIQUID FLUOROSILICONE RUBBER (FLSR)

Liquid silicone rubber (LSR) is designed to produce rubber parts more efficiently and economically. In general, LSR offers the fabricator faster cycle times, clean operations resulting from enclosed systems, and automated processing. Fluoro-silicone rubber is a high-performance elastomer particularly suited to environments where fuel, oil or solvent is present. Advances have been made in silicone rubber technologies that allow the process efficiencies of LSR to be coupled with much of the fluid resistance capabilities of fluorosilicone rubber. In the case of liquid VMQ silicone, even with a price premium typically realized (vs. HCR types), there are many advantages to the rubber fabricator, particularly in high volume parts. Even with the difference in price between the high consistency fluorosilicone, and liquid fluorosilicone rubbers, FLSR, the advantages of the liquid silicone product form justify its use. Fluorosilicone liquid rubber molding provides the ability to perform long runs with minimal manual intervention. Nearly unattended automatic operation is possible. In regions of the world with high labor costs, a single operator can maintain an entire bank of liquid injection molding machines.

CONCLUSIONS

We have developed an excellent understanding that allows us to recommend specific fluorosilicone rubber formulations capable of meeting the demanding requirements for turbocharger hose liners and other transportation applications.

Correct selection of the appropriate fluorosilicone base has been combined with formulation expertise in the areas of heat stability additives, secondary fillers and adhesion promoter technology. These building blocks have produced optimum results for physical property retention after relevant exposure to both dry heat and hot oil. Additionally, we have shown the physical properties of FVMQ to be much less sensitive to testing at elevated temperatures when compared to FKM.

Adhesion improvements have also been demonstrated to yield VMQ-FVMQ bond strengths comfortably in excess of typical specifications.

In summary, we now see a very exciting potential for these optimized FVMQ materials to satisfy the growing needs for both high temperature and hot oil resistance. This process should be facilitated by a close collaboration between potential customers and the FVMQ supplier.

The future is dynamic. The targets are constantly changing, and the demands to balance performance,
processing, and economics is more complex than ever. Even with fluorosilicone, the raw material price is just ONE component of the overall manufacturing cost. We must understand all the costs of producing parts. All process steps must be scrutinized and optimized (or eliminated). Question the status quo. Go beyond your personal comfort zone. Ask stupid questions (and remember that there are no stupid questions). When your supplier offers a product solution (for example) that will run faster or improve yield, you should understand the value that he/she is bringing to your company. The Purchasing Department will always look (first) to reduce the vendor’s product price. The Engineering Department must understand the overall business impact. The innovators in our business will thrive and grow. Those that try to hold on to what they had in the past will soon realize that all they have is smoke and memories.