Abstract

Fluorosilicones (FVMQs) are very competitive when used in applications requiring wide operating temperatures and fluid resistance. Their unique physical properties have never been in greater demand for applications in contact with jet/automotive fuels, solvents and/or engine oils. As more fabricators manufacture products using fluorosilicones and competition increases, Dow Corning’s high consistency fluorosilicone compound technology (FSR) has evolved to offer greater flexibility in meeting these requirements. At the same time, Dow Corning understood there were still unmet needs for fluorinated materials for use in liquid injection molding equipment.

Dimethyl based liquid silicone rubber (LSR) was initially developed to allow manufacturers to produce rubber parts more efficiently by providing fast cycle times, less contamination (closed system), material waste reduction, and automated processing. However, automotive parts fabricators and OEMs could not guarantee long term performance of LSR molded parts in certain environments due to insufficient resistance to fuel or other aggressive fluids.

To take advantage of the strengths of both technologies, Dow Corning has developed a new, fully fluorinated LSR that allows the process efficiencies of LSR to be integrated with the performance capabilities of FSR. Dow Corning has also expanded its product offering with copolymer and self-bleed versions. This paper will highlight the innovative possibilities and benefits of the new Silastic® brand F-LSR product series.
**Dow Corning FSRs and F-LSRs: Wide Use Temperatures and Fluid Resistance**

By completely substituting one of the two methyl groups on the siloxane backbone with a trifluoropropyl group, Dow Corning has developed new 100 mol% F-LSR products with similar mechanical and chemical resistant properties to FSR combined with the lower viscosity and processability of LSR. With 40 mol% substitution on the backbone, Dow Corning copolymer F-LSRs have enhanced rubber properties and fuel/oil resistance as compared to polymer blends. Polymer blends exhibit poor miscibility, whereas copolymers provide interactions at the molecular level. These new liquid trifluoropropylmethyl silicones and trifluoropropylmethyl dimethyl copolymer silicones have greater fluid resistance to fuels and oils than dimethyl silicones.

Fluorosilicones are very competitive in applications requiring wide operating temperatures and fluid resistance. In applications like turbocharger hose liners, the combination of high temperature stability, adhesion to dimethyl silicones and fluid resistance make fluorosilicones the natural choice. They are equally competitive when low use temperatures in presence of fluids make for harsh application conditions.

*Figure 1 - Fluorosilicones performance matrix*

<table>
<thead>
<tr>
<th>Hot</th>
<th>Cold</th>
<th>Fluids</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Fluorosilicone Not Typically Used</strong></td>
<td><strong>Fluorosilicone is Competitive</strong></td>
<td><strong>Fluorosilicone is Very Competitive</strong></td>
</tr>
</tbody>
</table>

The new *Silastic* 100% F-LSRs (trifluoropropylmethyl liquid silicone rubbers) share the following properties with the copolymer 40 mol% F-LSRs (trifluoropropylmethyl dimethyl liquid silicone rubbers):

- No post cure potential;
- Lower use temperature by elimination of polymer melt point (No Tm!),
  - Copolymer F-LSR Tg ~ -100°C,
  - 100% F-LSR Tg ~ -70°C;
- Wide temperature stability; and
- Good mechanical properties like tensile and tear strengths for excellent performance.

The new *Silastic* 100% F-LSRs offer these significant benefits over the copolymer series:

- Excellent resistance to non-polar hydrocarbon fuels, oils, and solvents
- Improved solubility in polar fluids such as esters and ketones
- Same fluid resistance as standard high consistency FSR grades
Both series have self-bleed versions available.

Figure 2 - Dow Corning’s new liquid Silastic rubbers by mol% of Trifluoropropylmethyl groups, trifluoropropyl groups lower use temperature while positively impacting fluid temperature to -115°C. Even 5.0 mol% trifluoropropyl groups on the siloxane backbone will limit polymers; however, the actual use temperature is prematurely limited by a melting point. The low temperature behavior of silicone rubber has been well documented. Silicone based Silastic rubbers by mol% of Trifluoropropylmethyl FL 30-9201 and Silastic FL 40-9201 to -100°C for Silastic FL 45-9001 and Silastic FL 65-9001.

Figure 3 - Glass transition temperatures (Tg) for silicone and fluorosilicone materials

The Silastic F-LSRs, especially the 100% grades, show good mechanical properties and low compression set values even without post curing, which makes them particularly suitable for sealing applications. Post curing can help to improve compression set while not substantial impacting other properties. Table 1 summarizes the properties for Silastic F-LSRs.
The four Silastic brand F-LSRs still performed well at -60°C, showing little change as compared to the room temperature data. The copolymer actually did not break within the limitations of the environmental chamber (>360 % elongation). The four F-LSRs were also tested at high temperature against ASTM D2000-06-03a Standard Classification System for Rubber Products in Automotive Applications, a classification system that arranges rubber properties into characteristic material designations. The first letter (type) is based on heat age resistance, and the second letter (class) is based on resistance to swelling in oil. The new Silastic F-LSRs perform well at very high temperatures. Remarkably, the copolymer F-LSRs have end use temperature windows of nearly 300°C!

ASTM fluid testing was done with IRM 903. Graph 1 shows the resistance of the different Silastic F-LSR grades to a wide variety of other fluids, and the very good swell resistances achieved over extended testing times. Note the very good swell resistance obtained in aggressive diesel type fluids. Good mechanical properties were retained throughout the aging tests, especially for the two Silastic 100% F-LSRs.
The effect of fluorine substitution is evident in the lower swell for the 100 mol% F-LSRs. This lower swell translates into lower permeation. Permeability was measured below in two different ways. First, a flat rubber sheet was clamped on top of the permeation cup containing the fuel to be evaluated and weight loss was measured. The permeation was done in Reference Fuel C with 10% Ethanol (CE10) at 60°C to highlight the differences in fluorosilicones and dimethyl silicone rubbers. The performance of the copolymer is significantly better than the dimethyl HCR while the Silastic 100% F-LSR and FSR have dramatically lower permeation rates.

Secondly, permeation was measured on O-rings under compression. Sheet testing does not take into account the actual gasket or o-ring configuration. The O-ring test fixture allows the evaluation of the effect of compression. The results in Graph 3 clearly demonstrate that the effect of compression varies from material to material. For example, after the initial decrease with 10% compression, both the Silastic 100% F-LSR and the FSR shows less permeation reduction from compression of the gasket than either the dimethyl or copolymer materials. The two fully fluorinated materials have significantly lower permeation and behave similarly.
Further testing of Silastic FL 40-9201 was also performed in various fuels and biofuels to evaluate the effects these fuels have on material performance. Testing was carried out for 1008 hrs at temperatures of 60°C. Table 3 summarizes the properties for Silastic FL 40-9201. This data shows the swell and mechanical performance achieved with Silastic F-LSRs. Based on the outstanding results achieved, these materials are well positioned to resolve some of the technical challenges that have prevented new solutions from being offered to the market.

Table 3 - Change in properties of Silastic FL 40-9201 in after 1008 hrs at 60°C

<table>
<thead>
<tr>
<th></th>
<th>ORIGINAL</th>
<th>DIESEL(1)</th>
<th>B20</th>
<th>FUEL C(2)</th>
<th>E25(4)</th>
<th>E85(5)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hardness,</td>
<td>35</td>
<td>0</td>
<td>-1</td>
<td>0</td>
<td>0</td>
<td>-1</td>
</tr>
<tr>
<td>Point Change</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tensile Strength</td>
<td>9.48</td>
<td>-14%</td>
<td>-17.50%</td>
<td>5.00%</td>
<td>-1.40%</td>
<td>-4.70%</td>
</tr>
<tr>
<td>% Change</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Elongation</td>
<td>459</td>
<td>-13%</td>
<td>-11.50%</td>
<td>3.30%</td>
<td>1.70%</td>
<td>-0.90%</td>
</tr>
<tr>
<td>% Change</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>100% Modulus,</td>
<td>0.85</td>
<td>10%</td>
<td>4.00%</td>
<td>0.00%</td>
<td>-5.90%</td>
<td>-5.90%</td>
</tr>
<tr>
<td>% Change</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Volume Swell,</td>
<td>n/a</td>
<td>4.20%</td>
<td>4.50%</td>
<td>24.70%</td>
<td>29.80%</td>
<td>11.70%</td>
</tr>
<tr>
<td>% Change</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Weight,</td>
<td>n/a</td>
<td>-1.30%</td>
<td>-1.80%</td>
<td>-1.30%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>% Change</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

(1) Diesel - 100% Reference Fuel F, tested "wet"
(2) B20 - 20% Soy Methyl Ester / 80% Reference Fuel F, tested "wet"
(3) Fuel C - 100% Reference Fuel C, tested after 72 hour / RT dry out
(4) E25 - 25% denatured ethanol / 75% Reference Fuel C, tested after 72 hour / RT dry out
(5) E85 - 85% denatured ethanol / 15% Reference Fuel C, tested after 72 hour / RT dry out

Fluorosilicones are used today in contact with transmission fluid. A FSR and two different Silastic F-LSR grades were aged for 1000 hrs at 150°C in ATF+4. The copolymer F-LSR was almost completely degraded, whereas the 100% F-LSR and the FSR still retained elastic properties despite tensile strength loss. The results in Table 4 show that the swelling is very low for both 100% grades.
Table 4 - Aging results after 1000 hrs at 150°C in Transmission Fluid ATF+4.

<table>
<thead>
<tr>
<th>FCM 45-49XX BLACK (High Consistency FSR)</th>
<th>FL 40-9201 (100% F-LSR)</th>
<th>F-LSR Copolymer</th>
</tr>
</thead>
<tbody>
<tr>
<td>Original</td>
<td>After Aging</td>
<td>Change</td>
</tr>
<tr>
<td>Durometer (Shore A)</td>
<td>41</td>
<td>48</td>
</tr>
<tr>
<td>Tensile Strength</td>
<td>8.6</td>
<td>3.4</td>
</tr>
<tr>
<td>Elongation (%)</td>
<td>458</td>
<td>244</td>
</tr>
<tr>
<td>Volume Swell (%)</td>
<td>0%</td>
<td>-0.60%</td>
</tr>
</tbody>
</table>

Using **Silastic** 100% F-LSR

Today, designers of fuel resistant parts are not constrained by processing limitations inherent to small or intricate parts. What makes liquid injection molding a better solution from a manufacturing standpoint is now available for fluorinated silicones. **Silastic** 100% F-LSR rubber processes like a dimethyl liquid silicone rubber, which means no special equipment or tooling is necessary. Standard LSR equipment can be used.

**Figure 4 - LSR injection molding equipment**

*Silastic* F-LSR is a unique offering incorporating the best of FSR and LSR to provide enhanced fuel resistance combined with improved processability. As such, it possesses the following characteristics:

- Low viscosity;
- Fast cycle time;
- Overmolding Capabilities;
- Long pot life; and
- Pigmentable.

Each of these properties will be discussed in more detail hereafter:
Low Viscosity

With Silastic 100% F-LSR’s lower viscosity as compared to other fluorinated elastomers, manufacturers can run production equipment faster and more efficiently. There are several immediate benefits from Silastic 100% F-LSR’s lower viscosity:

- Reduced injection pressure, higher fill speed;
- Freedom of design;
- Flashless articles; and
- Higher number of cavities in the mold.

When working with high consistency FSR, the material’s high viscosity often causes manufacturers to reduce temperatures in order to fill mold cavities completely without weld lines, flow lines, or scorch. This lower temperature increases curing time and decreases productivity. An additional issue with high consistency fluorosilicone rubber is incomplete cure. Because tool temperatures are often set lower to prevent premature curing before all material fills the cavity, the parts often look “lazy” and less snappy, which may cause manufacturers to increase cure time in order reduce laziness and decrease sticking to the mold.

Manufacturers will realize manufacturing efficiencies when changing to Silastic 100% F-LSR. The cure system used in these materials is designed to allow the material to flow into a mold before any significant increase in curing occurs. Once the mold is completely full, the material cures quickly.

*Figure 5 - Shear rate vs viscosity during processing*

Fast Cycle Time

Silastic 100% F-LSR from Dow Corning delivers extremely short cycle times while avoiding scorch, enhancing process productivity and production flexibility. This unique characteristic can allow lower mold temperatures while still maintaining reasonably short molding cycles. Peroxide cured FSR is more dependent on temperature to reach a high degree of cure. The rate of cure of peroxide cured FSR changes significantly based on temperature. With platinum cured Silastic F-LSRs, the rate of cure is much less influence by temperature. The slope of the
MDR curve only changes slightly with temperature as compared to peroxide cured FSR. This can be seen in Graph 4. This is particularly useful when attempting to overmold Silastic F-LSR onto an engineered plastic.

*Graph 4 - MDR curves for FSR and F-LSR at various temperatures*

![Graph 4 - MDR curves for FSR and F-LSR at various temperatures](image)

**Overmolding Capabilities**

The fast cycle times of the F-LSRs are not obtained at the expense of higher molding temperatures. As a liquid silicone rubber, it is possible to overmold Silastic F-LSR onto plastic parts. The overmolding can happen either in a separate operation or in a successive injection sequence in the same mold.

Overmolding processes can reduce the structure of the supply chain within the industry as many operations can now be integrated by either the silicone molder or the plastic molder. Overmolding will enhance manufacturing flexibility by:

- Saving time;
- Saving costs on shipment and stock of intermediate parts;
- Reducing quality assurance issues of incoming parts made elsewhere; and
- Removing the cost of assembling parts.

Considering current automotive trends for small engine designs and increased efficiency, environment focus and longer warranty periods, the increase in design flexibility as a result of innovative materials like these will be critical to meet market needs.

**Long Pot Life**

Pot life of liquid silicone rubber materials is a major concern for fabricators and manufacturers. A pot life of at least 3 days (taking into consideration a weekend shutdown) is necessary to ensure the mixed components inside molding equipment will still be pumpable upon startup. Silastic 100% F-LSRs meet this pot life requirement and; in many cases, testing has shown longer pot life than what can be achieved with LSRs.
Pigmentable

Silastic F-LSRs have been designed to be easily pigmented with many traditional dimethyl based LSR pigments. There is no significant impact on mechanical properties and processing when used at levels less than 2%. Higher levels of pigment addition should be evaluated on an individual basis. Table 5 summarizes the properties for Silastic FL 30-9201 without pigment and the addition of 2% pigment from two different LSR masterbatches.

Table 5 - Mechanical results for Silastic FL-30-9201 with and without pigment

<table>
<thead>
<tr>
<th></th>
<th>Non Post Cured</th>
<th>Post Cured</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>No Pigment</td>
<td>2% Loading Pigment #1</td>
</tr>
<tr>
<td>Duro (Shore A)</td>
<td>28</td>
<td>27</td>
</tr>
<tr>
<td>Comp Set (%)</td>
<td>23</td>
<td>24</td>
</tr>
<tr>
<td>Bayshore Resilience</td>
<td>22</td>
<td>21</td>
</tr>
<tr>
<td>Tensile Strength (psi)</td>
<td>1420</td>
<td>1350</td>
</tr>
<tr>
<td>Elongation (%)</td>
<td>490</td>
<td>525</td>
</tr>
<tr>
<td>100% Modulus (psi)</td>
<td>85</td>
<td>77</td>
</tr>
<tr>
<td>Tear (ppi)</td>
<td>102</td>
<td>112</td>
</tr>
</tbody>
</table>

Automotive Opportunities

Silastic F-LSRs enable manufacturers to manufacture seals, gaskets, diaphragms, grommets, intricate parts, and tighter tolerance components that offer a number of advantages.

Components manufactured with Silastic 100% F-LSR can withstand the harsh environment of oil and fuels, have limited swell when in contact with fuel and oil, and have a wide range of operational temperatures. This is especially important for applications in the automotive industry. In these applications, components must exhibit consistent functional performance whether the part is performing at -40°C during engine start up in the middle of winter or at 200°C continuous operation during the summer.

This new family of materials offers a number of advantages to automotive molders and part manufacturers:

Production with a standard liquid injection molding process can achieve three times higher productivity than with standard high consistency fluorosilicone rubber. This can be accomplished by:

- Less manpower per part produced;
- Flashless molding;
- No post cure cycles;
- Much shorter molding cycles with addition cure vulcanization;
- More cavities per tool than with high consistency rubber molding; and
- Molding and de-molding automation.
**Higher reliability** in performance of parts due to better process consistency and dimensional stability.

**Savings on maintenance costs** by using less pressure than required for FSR production. F-LSR production reduces stress on the injection machine and tool.

**Savings on investments** in molding equipment for present owners of liquid silicone injection molding machines. The dosing equipment is exactly the same as for standard LSR, and it can feed more than one injection machine.

**A better working environment** in plants as the Silastic F-LSR has no odor when curing. It is a platinum catalyst cure. In addition, there is no waste or flash when the process is designed properly which keeps the plant floor cleaner.

**Conclusion**

Dow Corning has offered one partially fluorinated LSR (trifluoropropylmethyl-dimethyl copolymer) for many years. This solution was not always satisfactory for many applications involving contact with fuel, oil, or solvents. In addition, it could only be supplied in red which prevented using it for applications requiring a specific color. Dow Corning has now united FSR and LSR technology with new 100% fluorinated liquid silicone technology that can be processed with standard liquid injection molding machines. This product line is further complimented by 40 mol% copolymer liquid silicone technology. Both of these technologies can be pigmented in a variety of colors. Dow Corning is now in a position to offer the market a family of materials that combines the best properties of high consistency FSR with the processing advantages of LSR.

The combination of chemical resistance, low temperature performance, processability, and fast cycle times make these new materials unique to designers, fabricators, and OEMs that are looking for innovative materials that help them differentiate their products and give a competitive advantage. Silastic brand F-LSRs offers the opportunity to innovate at the design level, realize new production efficiencies and produce small, intricate parts that withstand contact with aggressive fuels and oils while performing reliably under a range of extreme temperatures. Just another Silastic material from Dow Corning, just right for your application and processing conditions.

*Silastic* brand F-LSRs offers the opportunity to innovate at the design level, realize new production efficiencies and produce small, intricate parts that withstand contact with aggressive fuels and oils while performing reliably under a range of extreme temperatures. Just another *Silastic* material from Dow Corning, just right for your application and processing conditions.