Consumer Solutions

100% Fluoro Liquid Silicone Rubber: Fuel and Oil Resistance Achieved in an LSR
Unique Materials Unite the Best of FSR and Best of LSR

Marco Pagliani (Sesto – Italy), Emmanuel Bravais (Barry – UK), and Lauren Tonge (Midland, MI – USA)
Abstract
The unique physical properties of fluorosilicone rubber (FVMQs) have never been in greater demand. Used in applications requiring jet/automotive fuels, solvents and/or engine oils contact, fluorosilicones (FSRs) are increasingly finding use in a number of high-volume automotive applications. As more fabricators manufacture products using FSRs, process optimization and part yield become more important but still difficult issues. FSR compound technology from Dow has evolved to offer greater flexibility in meeting the requirements in standard rubber finishing equipment. At the same time, Dow has understood there were still unmet needs for a fluorinated material for use in liquid injection molding equipment.
Dimethyl based liquid silicone rubber (LSR) were initially developed to allow manufacturers to produce rubber parts more efficiently by providing fast cycle times, clean operation resulting from enclosed systems, material waste reduction, and automated processing. However, automotive parts fabricators and OEMs could not guarantee the long life 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 has developed a new, fully fluorinated LSR that allows the process efficiencies of LSR to be coupled with the performance capabilities of FSR. This paper will highlight the innovative possibilities and benefits of the SILASTIC™ brand F-LSR product range.

What is 100% F-LSR?
By completely substituting one of the two methyl groups on the siloxane backbone with a trifluoropropyl group, Dow has developed new F-LSR products with similar technical properties to FSR combined with the good flowability and processability of an LSR.

Graph 1: Dow’s new liquid SILASTIC™ rubbers by mol % of Trifluoropropylmethyl
Dow continues to expand the fluid resistance and durometer range of materials available to the market. The initial copolymer F-LSRs employ technology to enhance rubber properties and fuel/oil resistance compared to polymer blends. Polymer blends exhibit poor miscibility, while copolymers provide interactions at molecular level. The new SILASTIC™ 100% Fully Fluorinated Liquid Silicone Rubbers (F-LSRs) share the following properties with the copolymer F-LSRs:

- 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 range
- 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 SILASTIC™ F-LSR grades offer low temperature flexibility and high service temperature. Even five mole percent trifluoropropyl groups on the siloxane backbone will remove the low-temperature crystallization of dimethyl silicone at -40°C. The low temperature performance of the fluorinated series ranges from ~-70°C for SILASTIC™ FL 30-9201 and SILASTIC™ FL 40-9201 to -100°C for SILASTIC™ FL 45-9001 and SILASTIC™ FL 65-9001. The new SILASTIC™ F-LSRs also perform very well at very high temperatures.

Graph 2 shows the resistance of the different SILASTIC™ F-LSR grades to a wider variety of fluids and the very good swell resistances achieved over extended testing. Note the very good swell resistance obtained in aggressive diesel type fluids. Good mechanical properties were retained throughout the ageing tests, especially for the two SILASTIC™ 100% F-LSRs.

Graph 2: Volume swell for different fluid ageing tests

Table 1: ASTM 70 hour heat aging and oil aging test results
The effect of fluorine substitution is evident in the lower swell for the fully substituted materials. This lower swell translates into lower permeation. Permeability was measured below in two different ways. First, a 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. 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 4 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 both have significantly lower permeation and behave similarly again.
Table 2: Ageing results after 1000 hrs at 150°C in transmission fluid ATF+4

<table>
<thead>
<tr>
<th>Material</th>
<th>Durometer (Shore A)</th>
<th>Tensile Strength (MPa)</th>
<th>Elongation at Break (%)</th>
<th>Volume swell (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SILASTIC™ FCM 45-49XX BLACK (100% FSR)</td>
<td>41</td>
<td>8.6</td>
<td>458</td>
<td>0%</td>
</tr>
<tr>
<td>SILASTIC™ FL 40-9201 (100% F-LSR)</td>
<td>48</td>
<td>3.4</td>
<td>244</td>
<td>-0.60%</td>
</tr>
<tr>
<td>SILASTIC™ FL 45-9001 (F-LSR Copolymer)</td>
<td>41</td>
<td>10</td>
<td>366</td>
<td>4.60%</td>
</tr>
</tbody>
</table>

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<td>244</td>
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Two different SILASTIC™ F-LSR grades and a FSR were also aged for 1000 hrs at 150°C in the transmission fluid ATF+4. This is a very aggressive oil. The copolymer F-LSR was almost degraded, whereas the two SILASTIC™ 100% F-LSR and the FSR, despite tensile strength loss, still retain some elastic properties. The results in Table 2 show that the swelling is very low for both 100% grades.

In addition to the ageing data presented, the SILASTIC™ F-LSRs, especially the 100% grades, show good mechanical properties and low compression set even without post curing which makes them particularly suitable for sealing applications. Table 3 summarizes the properties for such SILASTIC™ F-LSRs. The swell and technical characteristics achieved with SILASTIC™ FL 30-9201 and SILASTIC™ FL 40-9201 resolve some of the technical challenges to offer new solutions to the market.

Table 3: Property summary for F-LSR grades

<table>
<thead>
<tr>
<th>Material</th>
<th>SILASTIC™ FL 45-9001</th>
<th>SILASTIC™ FL 65-9001</th>
<th>SILASTIC™ FL 30-9201</th>
<th>SILASTIC™ FL 40-9201</th>
</tr>
</thead>
<tbody>
<tr>
<td>Durometer</td>
<td>45</td>
<td>65</td>
<td>30</td>
<td>40</td>
</tr>
<tr>
<td>Swell – RFC</td>
<td>143</td>
<td>110</td>
<td>20</td>
<td>20</td>
</tr>
<tr>
<td>Swell – Oil</td>
<td>5-10</td>
<td>5-10</td>
<td>0-5</td>
<td>3</td>
</tr>
<tr>
<td>Tensile, psi</td>
<td>800</td>
<td>700</td>
<td>1200</td>
<td>1200</td>
</tr>
<tr>
<td>Tear B, ppi</td>
<td>100</td>
<td>70</td>
<td>90</td>
<td>100</td>
</tr>
<tr>
<td>Elongation</td>
<td>300</td>
<td>200</td>
<td>300</td>
<td>300</td>
</tr>
<tr>
<td>Comp Set 22 hrs @ 177°C</td>
<td>17(1)</td>
<td>17(1)</td>
<td>25(2)</td>
<td>30(2)</td>
</tr>
<tr>
<td>Extrusion Rate</td>
<td>125</td>
<td>100</td>
<td>65</td>
<td>25</td>
</tr>
</tbody>
</table>

(1) Properties obtained without post curing
(2) Properties obtained after post curing 4 hours at 200°C

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.
**Injection Molding Equipment**

**Mold**
- Temperature: 170 - 220°C
- Cold runner systems
- Hardened steel
- Exact finishing 1/1000 mm
- Dearing

**Injection Molding Machine**
- Standard injection molding machine
- Special LSR screw and barrel
- Hardened steel
- Spring loaded non-return-valve
- Cooled barrel to 23°C

**SILASTIC™ F-LSR**
- Pourable to paste
- 2-component
- 1:1 mixing ratio
- Supply in 20 1 pails or 200 1 drums

**Pump / Mixer**
- Hydraulic or pneumatic
- Pressure 180 - 220 bar
- Trough static mixer
- Plus color additive

SILASTIC™ F-LSR is a unique combination of the best of FSR and the best of LSR to provide enhanced fuel resistance in combination with the improved processability of liquid silicone rubber:
- Very low viscosity
- Fast cycle time
- Long pot life
- Overmolding capabilities

Each of these properties are discussed in more detail hereafter:

**Low Viscosity**

Because of the viscosity decrease realized when changing to SILASTIC™ 100% F-LSR, manufacturers can run production equipment faster and better. There are several immediate benefits from SILASTIC™ 100% F-LSR’s lower viscosity:
- Reduced process conditions set up (pressure and speed)
- Flashless articles
- Higher number of cavities in the mold

**Processability**

![Processability Diagram](image)
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 or flow lines. This lower temperature increases curing time and decreases productivity. Manufacturers will realize manufacturing efficiencies when changing to SILASTIC™ 100% F-LSR. Tool temperature can be set higher, improving curing degree and reducing temperature impact on final properties, as well as reducing vulcanization time.

An additional issue with solid fluoro silicone rubber is incomplete cure. Because of tool temperature set up on the edge, parts often look “lazy” and less snappy, which may cause manufacturers to increase cure time in order reduce laziness and improve stickiness on the mold.

**Fast Cycle Time**

SILASTIC™ 100% F-LSR from Dow delivers extremely short cycle times, enhancing process productivity and production flexibility. This property can help to work with lower temperatures of the mold maintaining reasonable short molding cycles. This is particularly useful when attempting to overmold SILASTIC™ F-LSR onto an engineered plastic.

**Long Pot Life**

Pot life of liquid materials is a major concern for fabricators and manufacturers. Considering the fast curing behavior when the two components are mixed together, it is necessary to ensure that after the weekend the material mixed inside molding equipment would be still pumpable with no need to purge fresh material out. The pot life of SILASTIC™ 100% F-LSR is longer than what standard LSRs can ensure.

**Overmolding Capabilities**

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 in the same mold.

Overmolding processes will slim 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:

- Saving time
- Saving costs on shipment and stock of intermediate parts
- Reduce quality assurance issues of incoming parts made elsewhere
- Remove the cost of assembling parts

Considering current automotive trends for small engine designs and increased efficiency, environment focus and longer warranty needs, the design of parts will be fundamental and having an innovative material will be the key to match market solutions.

**Automotive Opportunities**

Fluoro liquid silicone rubber enables manufacturers to manufacture seals, gaskets, diaphragms, grommets, three-dimensional parts, smaller parts, intricate parts and dimensionally more precise 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 characteristics whether they are sitting in cold climates, staying idle in the cold or heating up when running during summer months.

Fluoro liquid silicone rubber offers a number of advantages to automotive molders and part manufacturers:

- **Higher productivity** is achieved with a standard liquid injection molding process. We can reach three times higher productivity than standard solid fluorosilicone rubber with:
  - Less manpower per part produced
  - No manpower needed for post-molding handling
  - Flashless molding process is applicable
  - No post cure cycles
  - Much shorter molding cycles with additional cure vulcanization
  - More cavities per tool than with high consistency rubber molding
  - Molding and de-molding automatization due to the similar rheology of SILASTIC™ F-LSR and standard LSRs

**Higher reliability** of parts in use due to better homogeneity and dimensional precision.

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

**Savings on investments** in molding equipment for present owners of liquid silicone IMM (injection molding machine). 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 workshops as the SILASTIC™ F-LSR has no odor when curing. It is a platinum catalyst cure.
Conclusion

Dow has been offering partially fluorinated liquid rubber solutions for many years with trifluoropropylmethyl-dimethyl co-polymer LSR grades. These solutions were not fully satisfactory for some harsh applications. Dow has now united FSR and LSR technology with new 100% fluorinated liquid silicone technology that can be processed with standard liquid injection molding machines. We are now in a position to offer the market the best of high consistency FSR properties and the best of LSR for processing in one material.

As part manufacturers discover the benefits of SILASTIC™ F-LSR, the demand for further development will be considered by Dow to expand the SILASTIC™ liquid product range further in the following directions:

- Higher shore A hardness
- Self lubricating SILASTIC™ F-LSR
- Self adhering SILASTIC™ F-LSR
- Special grades for applications in the automotive, aviation, electrical industries

SILASTIC™ 100% F-LSR offers automotive manufacturers 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.