

Research Progress in Calenderable Fluorosilicone with Excellent Fuel Resistance

Haibing Zhang, Ph.D.
Andy Cloud
Arlon Silicone Technologies Division
1100 Governor Lea Road
Bear, DE 19701
302-834-2100

Abstract

Fluorosilicone rubber (FSR) is a high performance elastomer for applications requiring low temperature flexibility, high temperature stability, and fuel resistance. This paper describes the relationship between the fluorosilicone chemical structure and material properties. In terms of fuel resistance and low temperature flexibility, fluorosilicone is compared to other elastomers such as fluorocarbon rubber (FKM) and standard silicone rubber (MQ/VMQ/PVMQ). The application advantages and disadvantages of utilizing fluorosilicones are discussed. Arlon has developed a cost effective, calenderable fluorosilicone compound with both low viscosity and excellent fuel resistance. The calendered membrane is available in either reinforced or non-reinforced constructions for use in many applications, but specifically for fuel resistant diaphragms.

KEY WORDS: Silicone, Fluorosilicone, Fuel Resistance

1. Introduction

The chemical structure for the standard polysiloxane (MQ) is as shown in **Figure 1**:

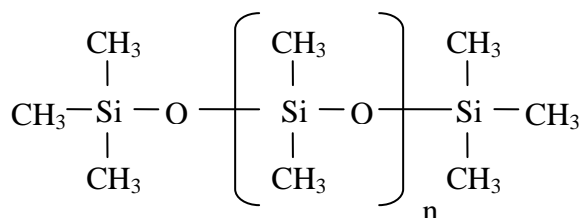


Figure 1 The chemical structure of a standard polysiloxane

As found in other polymers, copolymers of siloxanes play an important role in the technology of silicone rubber. While the backbone of silicone rubber is silicon-oxygen, the pendant groups can be methyl (MQ, most popular), vinyl methyl (VMQ, higher peroxide crosslinking efficiency), phenyl vinyl methyl (PVMQ, crystallization inhibition, low temperature flexibility), hydrogen (platinum crosslinking), and trifluoropropyl (FSR, solvent/fluid resistance) as shown in **Figure 2**.¹⁻²

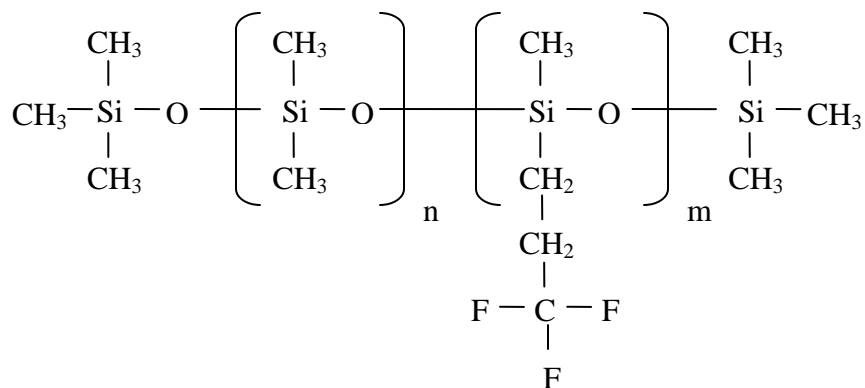


Figure 2 The chemical structure of fluorosilicone

2. The mechanism of dissolving

In the process of solvation, the solute and solvent are mixed to form a uniform solution. The solvation process is reversible. The solute can be recovered from a solution by evaporation, although it will not always be in the exact form that it was initially. For most of substances, there is a limit to the quantity of solute that dissolves in a specific quantity of solvent.

The common principle of solvation is “Like Dissolves Like.” It is a general rule describing the fact that polar substances are more likely to dissolve in polar solvents and non polar substances are more likely to dissolve in non polar solvents. The polar solute molecules have a positive and a negative end to the molecule. If the solvent molecule is also polar, then positive ends of solvent molecules will attract negative ends of the solute molecules. This is a type of intermolecular force known as dipole-dipole interaction. All molecules also have weak intermolecular forces called London Dispersion forces. For London Dispersion forces the positive nuclei of the solute molecule atoms will attract the negative electrons of the solvent molecule atoms. This gives the non-polar solvent greater ability to solvate the solute molecules.

While an uncured rubber or elastomer can be dissolved in a solvent, the cured rubber can only be swelled by the solvent, as shown in **Figure 3**. It is similar to a sponge in water. When small molecules of solvent penetrate into the rubber, the crosslink between polymer molecule chains of cured rubber limit the diffusion of polymer molecules into the solvent. The swelling will reach a dynamic equilibrium with time. After the dynamic equilibrium is reached, the solvent content in the rubber will remain constant.

If a fluid affects a cured silicone rubber after prolonged immersion, possibly at an elevated temperature, the physical property changes generally include either an increase or decrease in volume, hardness, tensile strength, and elongation. At a specific test temperature the effects of solvent or fuel immersion proceed until they reach a limit and increase no further. The limit is the maximum amount of solvent or fuel that the rubber can absorb. At a higher temperature the effects of solvent or fuel can become severe. While a solvent or fuel may produce little effect at room temperature, it may cause a significant change at elevated temperature. A swelling or

volume change caused by fluid penetration into the rubber is usually the most obvious effect. However, the swelling does not necessarily result in permanent deterioration. The rubber often regains most of its original properties after the solvent or fuel evaporates.³

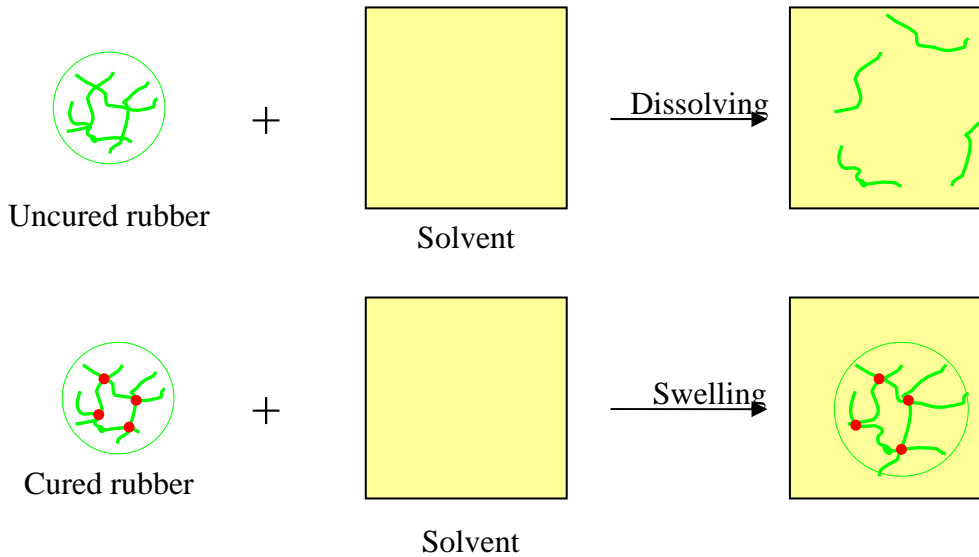


Figure 3 The schematic of the dissolving and swelling of rubber in solvent

3. The properties, fabrication, and applications of fluorosilicone

3.1 The properties of fluorosilicone

Since the introduction of poly (trifluoropropyl) methylsiloxane or fluorosilicone (FSR) as a commercial product in 1957, there has been an ongoing interest in siloxane polymer chemistry. FSR is most noted for applications that require low and high temperature performance in contact with jet and automotive fuels, many solvents, and engine oils.^{2-4, 7}

- **FSR versus other silicones**

Due to the extremely polar fluorine element in the chemical structure of FSR, FSR shows superior resistance to many fluids. The higher the aromatic or phenyl content of oils and fuels, the greater is their effect on other types of silicone (MQ/VMQ/PVMQ). However, (MQ/VMQ/PVMQ) silicones offer better resistance to acetone, other ketones, and some esters.⁴

FSR can be blended with other silicones to obtain a fluid resistance that is intermediate between the two polymer types. Since FSR has a significantly higher cost than other silicones, blending FSR with other silicones can potentially reduce costs if the blend is able to meet application requirements. Furthermore, although FSR has better low temperature flexibility than other rubbers such as FKM, blending with VMQ/PVMQ can further improve its low temperature flexibility.^{3, 7}

• FSR versus FKM

Fluorocarbon rubber (FKM) has higher fluorine content (up to 70%) than fluorosilicone (45%).^{5, 8} Fluorocarbon rubber is unequalled in chemical and fluid resistance and is generally used in applications requiring excellent thermal stability and outstanding sealing capability. These applications include automotive, petroleum, and energy-related industries. Higher fluorine content in fluorocarbon rubber correlates to lower volume swell.⁵

However, FKM ($T_g = -15^\circ\text{C}$, by DMA method) has a relatively high glass transition temperature compared to FSR ($T_g = -55^\circ\text{C}$, by DMA method). Poor low-temperature flexibility limits the use of FKM in many application areas.⁷ Extremely high FKM viscosity leads to poor flow characteristics and limits processing to the compression and transfer molding. Moreover, a study conducted by Dow Corning and Rapra also found that in high temperature applications up to 200°C , the tear strength and elongation of FSR is significantly better than FKM, while the tensile strength of FKM and FSR are comparable.⁷

3.2 The fabrications of FSR

FSR can be fabricated by compression molding, transfer molding, injection molding, extrusion, and calendaring.^{4, 9} The FSR compound presents unique challenges for matching particular compounding technologies to various fabrication processes. For example, a FSR compound that works for extrusion may not work for calendaring. The FSR products supplied from different manufacturers or compounders for the purpose of meeting certain specifications may ultimately show completely different processing properties on specific equipment.

Basic compounding ingredients for FSR include:^{4, 7}

- 1) **Pure FSR gum.** FSR from different manufacturers has varying mechanical and chemical properties due to varying molecular weights, trifluoropropyl content, and vinyl content. The different gums enable custom bases to be created and tailored to meet exact performance and cost target profiles required for each application. Blending with VMQ can reduce cost provided the blend can meet the fuel resistance requirements. The viscosity of FSR gum also determines its processing properties. Based on viscosity, FSR can be classified into two product forms: a high consistency rubber form (HCR) and a liquid silicone rubber form (LSR). The LSR form allows for rapid processing in unattended injection molding machines.
- 2) **Fillers.** As with VMQ, fillers in FSR general include fumed, precipitated or ground silica. Fumed silica acts as a reinforcing agent, while other fillers are extending in nature and are used to meet the specifications of fluid resistance and economic targets. Structuring or Crepe Hardening (viscosity of silicone filled with silica increases with compound storage time) of a silica filled FSR compound occurs more slowly than a similarly filled VMQ compound.
- 3) **Curing agents.** Peroxides are commonly used for both FSR and VMQ siloxanes. For example, bis (2,4-dichlorobenzoyl) peroxide for low temperature, hot-air curing; benzoyl peroxide, dicumyl peroxide and 2,5-dimethyl-2,5di(t-butylperoxy) hexane for molding and steam curing manufacturing processes. Lastly, platinum salts can be used as another option for addition curing FSR.
- 4) **Other ingredients** such as pigments, process aids, and coupling agents can also be added into a compound to meet processing and final property requirements.

An FSR compound can be mixed on a two-roll mill for low volume manufacturing or in a dough or internal mixer for high volume manufacturing. The mixing of FSR compounds usually generates more heat than VMQ, and due to the sensitivity of some peroxides, it is important to keep all mixing equipment cool.

3.3 The applications of FSR

FSR has been used in demanding applications in which fuel resistance, low temperature performance, and high temperature performance are required. Beginning with its use in the aerospace industry and followed by its expansion into automotive applications, FSR has always been considered a premium, high priced product.⁷ The specific applications of FSR are seals, diaphragms, and other high performance rubber parts, such as

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

4. Experimental

4.1 Materials preparation

The formulations of fluorosilicone are mixed on a two-roll mill at room temperature. ASTM slabs are prepared by press curing (121°C for 20minutes) for the fuel resistance test.

4.2 Plasticity

The plasticity of the uncured compound is tested per ASTM D926. The unit of measurement is 1/100th mm. The plasticity test is a simple viscosity test for uncured rubber compounds to determine processing parameters. Higher plasticity correlates to higher polymer viscosity.

4.3 Fuel resistance

Fuel resistance or fuel swelling of Fuel A, Fuel C, and Fuel CM85 is tested per ASTM D471. In the case of Fuel A (isooctane), FSR samples are immersed at room temperature for 24 hours. In the case of Fuel C (isooctane: 50% by volume, toluene: 50% by volume) and CM85 (Fuel C: 15% by volume, anhydrous methanol: 85% by volume), FSR samples are immersed at 65°C for 48 hours under pressure. The unit of measurement is percent volume change.

5. Result and discussion

For calendering an FSR compound, either a 3-roll or 4-roll calender may be used. Processing long, continuous, uniformly thick sheets are the main advantages of the calendering process. As a leader in precision calendered silicone, Arlon can process fluorosilicone with a uniform thickness as thin as 2 mils. Due to the continuous process, a 50” wide web can be calendered to a finished length of 1000 yards. This significantly reduces the processing cost. The calendered FSR can also be reinforced with fiberglass, polyester, or other polymeric fabrics.

Compared to molding (press, transfer, injection) and extrusion, calendering has a more stringent requirement for the processing properties of the FSR compound. The main reasons include:

- 1) **High FSR viscosity.** FSR has a higher viscosity than other silicones (MQ/VMQ/PVMQ). High viscosity constrains the FSR processing window, especially when thickness tolerance is stringent.
- 2) **Hot-air or Infrared curing.** This limits the use of peroxides. Not all peroxides can be used for an in-line curing process..
- 3) **Fabric adhesion.** When fiberglass or polyester fabric is used to reinforce FSR, standard VMQ adhesion promoters will not be applicable for the FSR. New prime coatings need to be utilized.

Arlon has overcome these difficulties through a new FSR compound with low viscosity or plasticity. The new FSR compound has excellent fuel resistance (specifically Fuel A, Fuel C, and Fuel CM85). In the following table, the properties of Arlon’s new FSR compound are compared to FSR compounds from several top vendors in the silicone industry.

Table 1 The result of plasticity and fuel resistance

Formulation no.	Supplier	Plasticity (1/100mm)	Fuel A swelling (v%)	Fuel C swelling (v%)	Fuel CM85 swelling (v%)
FSR-1	S-1	417	6.9	17.1	9.0
FSR-2	S-1	337	11.6	27.8	7.9
FSR-3	S-2	381	12.7	28.6	13.1
FSR-4	S-2	324	15.8	28.5	12.4
FSR-5	S-3	562	N/A	N/A	N/A
FSR-6	S-3	373	9.2	24.9	10.8
FSR-7	S-3	340	16.0	43.3	10.7
FSR-8	S-3	341	8.4	N/A	N/A
FSR-9	S-4	443	14.8	31.1	Dissolved
FSR-10	S-4	344	16.4	28.6	Dissolved
FSR-11	S-5	665	N/A	N/A	N/A
FSR-12	S-5	308	13.5	32.9	11.1
FSR-final	Arlon	354	6.0	18.7	11.9

The calendering process at Arlon generally requires a plasticity lower than 375 (1/100mm). Five FSR compounds (FSR-1, FSR-3, FSR-5, FSR-9, FSR-11) were evaluated from five different suppliers. All of the compounds had a plasticity higher than 400 (1/100mm). The cured FSR-9 dissolved in fuel CM85 for an unknown reason. The requirement for Fuel C and CM85 is no physical deterioration.

After feedback was provided to the various suppliers, a second round of compounds (FSR-2, FSR-4, FSR-6, FSR-10, FSR-12) were evaluated. While the plasticity of these samples passed the requirement, fuel A volume swell was significantly higher than the original materials evaluated. All of the compounds had very high Fuel C volume swell. The second round compound from supplier V-4 (FSR-10) again like (FSR-9) dissolved in Fuel CM85 for an unknown reason. The third and fourth round of compounds evaluated from V-3 did meet the plasticity requirement, but the fuel A volume swell remained higher than the requirement.

Working with supplier V-1, chemists at Arlon developed a new FSR formulation (FSR-final). FSR-final was chosen as the best formulation for production calendering. It has the lowest volume swell in Fuel A and the second lowest volume swell in Fuel C. It also has a favorable plasticity and an acceptable amount of swell in fuel CM85. Moreover, FSR-final is the most cost effective FSR compound in the entire group being evaluated. (FSR-1---FSR-12).

6. Conclusions

Fluorosilicone rubber (FSR) can be used in applications requiring low temperature flexibility, high temperature stability, and fuel resistance. Compared to fluorocarbon rubber (FKM) and silicone rubber, FSR has advantages in terms of processing properties, fuel resistance, and low temperature flexibility. Arlon has developed a calenderable FSR compound with both low viscosity and excellent fuel resistance. Arlon's FSR compound is a cost effective option versus other commercially available FSR on the silicone market. Materials can be calendered between 2 to 60 mils thickness and is available in reinforced or non-reinforced constructions for use in many applications, but specifically for fuel resistant diaphragms.

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