Overview of Fluorosilicone

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Abstract

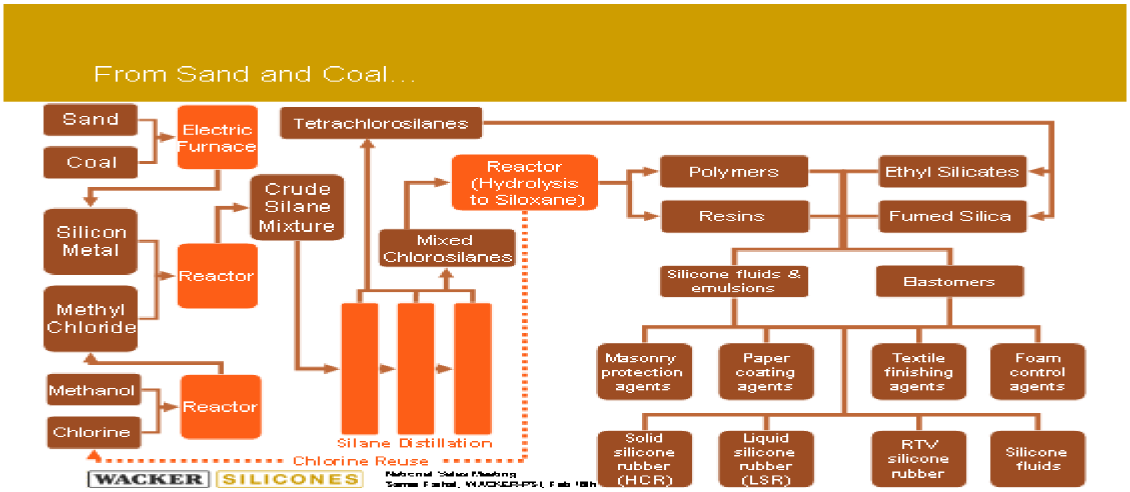
Silicones are known for their application along a wide range of temperature, the widest of the commercially available polymers. They are, however, susceptible to degradation by hydrocarbons and permeation of vapors. Fluorocarbons are high strength, low permeation materials with fairly good high temperature resistance, but limited low temperature application. Both elastomers are considered specialty polymers, and they are priced accordingly, the fluorocarbons being the most expensive. When looking at the similarities and differences of these two materials, the hope exists to gain the best of both at a lower price than the premium paid for fluorocarbon. The development of fluorosilicones is intended to do provide an approach to accomplish that goal.

Introduction

Few polymers provide adequate performance at temperatures above 150 ℃. Of these, only silicone and fluorocarbon approach or exceed 200 °C. Each of these materials possess other performance properties that differentiate them from one another. Fluorocarbon is a very tough – high tensile strength, tear strength, and abrasion resistance – material that has excellent resistance to gas permeability. Silicone is a more elastic – high elongation – material that is also very flexible at low temperatures. In fact, silicone possesses the widest operating range of any polymeric material. Continuous operating temperatures of 225 ℃ may be withstood, while the same part may rema in flexible down to temperatures as low as – 40 ℃. With proper additive packages, the upper or lower ends of this temperature range may be extended. In addition, new studies are underway to show that silicone maintains a higher percentage of its original physical properties at usage temperature than do the other polymeric materials.

With such abilities for usage range one might wonder why silicone is not the most widely used elastomer. Like all other elastomers, silicone has certain weaknesses. The first of these, in relation to other organic polymers, is its fairly high price. Derived from sand that must be cleaved to yield the silicon metal building block, the process stream that leads to the finished silicone polymer is long and expensive (Fig 1).

Figure 1



The cost of silicone can approach that of double some of the organic elastomers, leaving fluorocarbons as one of the few materials over which silicone maintains a price advantage.

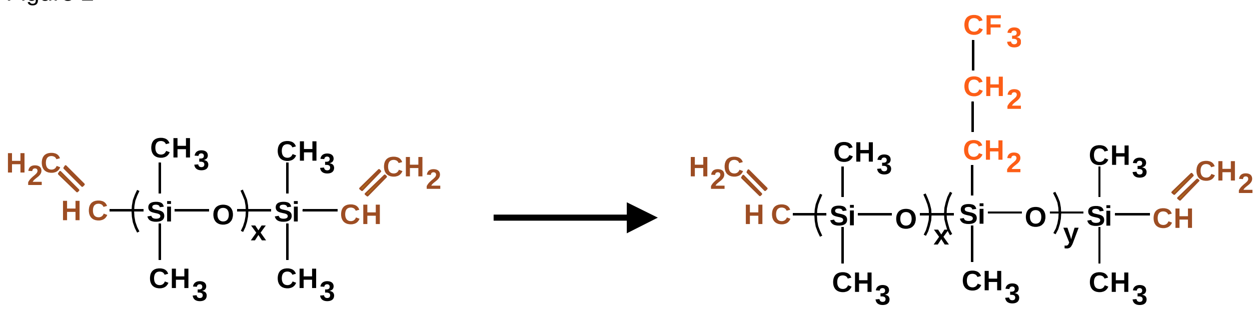
The second reason for the lack of greater use of silicone is directly related to its ability to meet application demands. For example, automotive engine systems utilize many hydrocarbon and petroleum derived lubricating oils which attack the structure of the silicone polymer. This results in loss of physical strength and elasticity as well as in high swell. Another automotive related application is contact with fuel and/or vapor. The lack of permeability resistance yields very high swells and the ability for the vapors to escape to the surrounding environment. Reduction of this vapor loss is currently a major emphasis of governmental regulating bodies. It is in these same areas that fluorocarbons perform well, and which provided the impetus for the development of fluorosilicones.

Initial Fluorosilicone Development

The idea behind the development of fluorosilicones was the desire to impart some of the chemical resistance seen in fluorocarbons by adding a fluoro moiety to the silicone chain at a price below that of fluorocarbons. This was accomplished by replacement of the some of the methyl groups with trifluoropropyl groups at the polydimethylsiloxane backbone (Fig. 2). With this came increased flexibility within the industry to balance the performance needs with the cost of the elastomer chosen. As can be seen in Table 1, the goal of improving the properties of silicone is realized, especially in the area of hydrocarbon resistance. This is achieved with only a minor trade off of a slightly higher low-temperature limit.

The blend of properties held by fluorosilicone make it well suited for applications that were once off limits to silicone. Transmission and engine gaskets of all kinds that see hydrocarbons with or without the possibility of short term fuel exposure. High heat applications not requiring the full permeability resistance of fluorocarbons. Traditional automotive wire seals and connectors that may be contacted by oils or hydrocarbons. The same for wire seals and connectors for aerospace, where the wide temperature range is especially important.

Figure 2



VMQ: Vinyl Methyl Silicone FVMQ: Fluoro Vinyl Methyl Silicone

Table 1

	VMQ	FVMQ	FKM
Low/High Temp Limits F	**-90** TO 450	**-70** to 400	-40 TO 400
Tensile Strength	P	P	**F**
Elongation	800	600	300
Hardness Range	20-80	40-80	45-90
Resilience-Rebound	F-G	G	F-G
Compression Set	G-E	G-E	G
Adhesion	G-E	F-P	F-G
Abrasion Resistance	P	P	**G**
Tear Resistance	P	P-F	F-G
Weather Resistance	E	E	E
Ozone Resistance	E	E	E
Water Swell Resistance	E	E	G
Steam Resistance	F-P	P	P
Gas Permeability	P	P	**G-E**
Acid Resistance	P-G	G	E
Alkali Resistance	E	F-E	F-G
Alcohols	G-E	G	F-G
Petroleum Oils	**P**	**E**	**E**
Aliphatic Hydrocarbons	**P**	**F-G**	**E**
Aromatic Hydrocarbons	**P**	**F-G**	**E**
Halogenated Hydrocarbons	P	F-P	**E**
Phosphate Ester	P	F-P	P
Polar Solvents	P	P	P

New Fluorosilicone Development

Standard, high-consistency, silicone rubber resembles the physical state of other polymers at room temperature. Liquid silicone rubber (LSR), silicone in a much more flowable state at room temperature, has been a growing segment within the silicone family for more than a decade. LSR is possible by formulating silicone rubber out of silicone fluids, as well as polymers, to meet the same demands and applications as high-consistency silicone. The application of this same technology has been applied to fluorosilicones in recent years. This advancement brings with it some major advantages over the previous processing techniques of high-consistency fluorosilicone. First and foremost, is the reduction in cycle time due to the addition-curing (platinum catalyzed) mechanism employed in LSR. Best utilized for smaller parts, the gains that are realized with a 30 – 40 second cure cycle can easily make up for the price premium paid for LSR.

A second advantage of LSR is the increased process control the more flowable material allows. This imparts the ability to more precisely fill out each cavity of the tool for improved part quality and reduced scrap. Coupled with advanced technologies now available in mold design, LSR avails itself to part production with very little or no flash and very small runners. This is an obvious materials savings, but also adds to the increased quality and the reduction of bad parts that are produced. Along with the addition of automated demolding apparatus, this allows for little oversight of the molding process, reducing labor at the press. In many cases, the parts need little or no inspection, some being boxed up right at the press, further reducing labor and secondary operations. The overall effect is that, when done with proper planning, the initial higher outlay of capital and the higher price of the LSR material are overcome and the overall piece price is reduced.

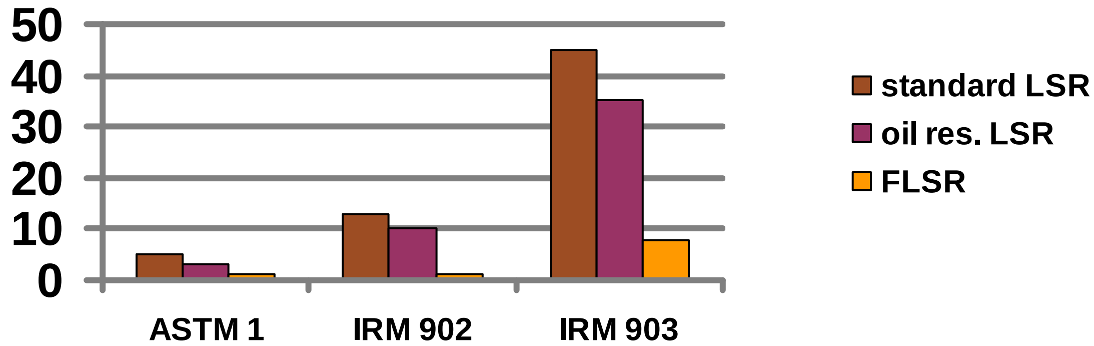
The combination of the improvement in hydrocarbon resistance in fluorosilicone with the advancements made in liquid rubber processing can be seen with the new products now on the market. Fluoro chemistry imparts the same improvement in chemical resistance to liquid silicone rubber as was seen for high-consistency materials (Tables 2 and 3). Although there is improvement in the resistance to standard reference fuels, the resistance to diesel and biodiesel are more applicable. Other significant improvements are seen in resistance to engine oils and automatic transmission fluids. As more diesels are offered and further advancements in biofuels are seen, the importance of liquid fluorosilicone will increase.

Table 2

`		LSR	FLRS
Mineral oil ASTM 1		6%	1%
Mineral oil IRM 903		43%	9%
BP engine oil C-20		22%	6%
Castrol SLX 0W30		25%	2%
Transmission oil BOT 154		33%	6%
Transmission oil ATF 3		45%	7%
FAM A	Toluene Isooctane Diisobutylene	215%	137%
Fuel C	Isooctane Toluene	208%	132%
Toluene		168%	79%

Gasoline		194%	78%
Diesel		53%	22%
Biodiesel (Rapsmethylester)		64%	29%

Table 3



Summary

Fluorosilicones were developed to improve the chemical resistance of silicones to hydrocarbons and vapor permeation. With a goal of being priced between that of standard silicones and fluorocarbons, it was hoped that the property improvements from that of standard silicone would approach that of fluorocarbons. With the proper substitution of trifluoropropyl groups for methyl groups on the backbone, this became a reality. The more recent application of liquid rubber technology to fluorosilicone imparts another positive attribute. Now, whether through performance, material cost, or the advantages derived from LSR processing, the opportunity for fluorosilicone to be the elastomer of choice continues to increase.