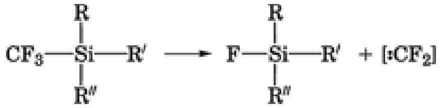
POLY(FLUOROSILICONES)

1. Introduction

The poly(fluorosilicones) are siloxane polymers with fluorinated organic substituents bonded to silicon. Poly(fluorosilicones) have unique properties resulting from the combination provided by fluorine substitution in the side groups and the siloxane polymer backbone structure (see SILICONES). The presence of carbon–fluorine bonds in organic polymers is known to impart polymer stability and solvent resistance. The larger electronegative fluorine atom gives strong C–F bonds and decreases the accessibility of the backbone to potential reactants. Substituting fluorine for hydrogen generally decreases solubility and surface energy and increases resistance to chemical attack and thermal stability. (1) Poly(fluorosilicones) are the only materials that combine high resistance to fuels, oils and solvents with the high resilience, low temperature performance, and outstanding ozone and weathering of silicone. (2)

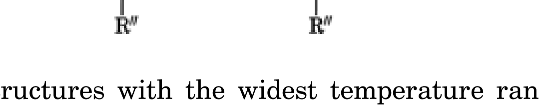
Many physical properties and features of poly(fluorosilicones) can be traced to their molecular structure. Polymer based solely on carbon and fluorine have a very compact structure with limited flexibility when compared to a fluorosilicones. Siloxane materials have long bond length and wide bond angles thus a high degree of unit rotation about the Si–O–Si bonds (Table 1). These features allow very low temperature flexibility and a high degree of free volume.

Commercially interesting poly(fluorosilicones) have at least one CF_3 group per silicon in their structure. The incorporation of a single carbon–fluorine bond into a polymer does not provide the stability and solvent resistance offered by substituents like the CF_3, C_2F_5, or C_3F_7 groups. The proximity of silicon and fluorine in such compounds governs the stability of the structure. Thermal rearrangement (eq. 1) occurs when fluorine is alpha to silicon. The thermodynamically more stable silicon–fluorine bond and difluoromethylene are formed. Difluoromethylene undergoes further chemistry characteristic of divalent carbon compounds.



$$CF_3{-}\overset{\overset{R}{|}}{\underset{\underset{R''}{|}}{Si}}{-}R' \longrightarrow F{-}\overset{\overset{R}{|}}{\underset{\underset{R''}{|}}{Si}}{-}R' + [{:}CF_2] \qquad (1)$$

When fluorine is beta to silicon, compounds undergo a facile elimination of an ethylenic compound again to form a stable silicon–fluorine bond (eq. 2).



$$CF_3CH_2{-}\overset{\overset{R}{|}}{\underset{\underset{R''}{|}}{Si}}{-}R' \longrightarrow F{-}\overset{\overset{R}{|}}{\underset{\underset{R''}{|}}{Si}}{-}R' + CF_2{=}CH_2 \qquad (2)$$

Structures with the widest temperature range of demonstrated stability have fluorine at least in the gamma position relative to silicon, as in $CF_3CH_2CH_2SiRR''R''''$. Longer hydrocarbon chains, with or without hetero atoms, are feasible, but oxidative stability (attack of CH_2) is compromised and such materials are generally disfavored. Longer fluorinated substituents are required for the lowest possible surface energy (4). Poly(3,3,3-trifluoropropyl)-methylsiloxane [26702-40-9] demonstrates this structural principle and is a key family of industrial fluorosilicone materials. Copolymers with polydimethylsiloxane are available to balance properties with the cost of fluorine substitution.

2. Properties

2.1. Fluid and Chemical Resistance. Fluorosilicones are especially suited for applications involving repeated exposure to fuels, oils, hydraulic fluids, and various chemicals (5). Fluid resistance is excellent to almost all solvents including alcohol–hydrocarbon mixtures currently being evaluated as alternative fuels. Even at elevated temperatures, prolonged immersion causes only slight elastomer swelling. Exceptions to this rule are highly polar solvents, such as esters and ketones.

2.2. Heat Resistance. Fluorosilicone elastomers have long-lasting dependability in static and dynamic applications over a wide range of temperature. Thermal cycling does not lead to embrittlement. Service temperatures range from −60 to 200°C. Certain fluorosilicone elastomers can handle short-term service temperatures (hours) up to 250°C with little change in hardness; brief exposures up to 260°C result in retention of about 50% of the original tensile strength. From 120°C to the upper service temperature at 200°C, fluorosilicone elastomers exhibit properties equal to or better than fluorocarbon elastomers (6).

2.3. Low Temperature Properties. Poly(3,3,3-trifluoropropyl)methylsiloxane has a glass transition temperature (T_g) of −75°C. Fluorosilicones do not crystallize like polydimethylsiloxanes. Low temperature elastomeric properties have been measured including: brittleness temperature by impact (ASTM D746B) of −59°C and TR10 (ASTM D1329) of −50°C, which are considerably lower than for fluorocarbon elastomers (7).

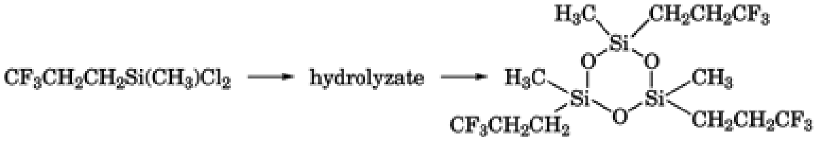
2.4. Electrical Properties. Fluorosilicone elastomers have inherently good electrical insulating properties, like their unfluorinated silicone counterparts. The dielectric properties remain relatively unchanged when the elastomer is exposed to severe environments (2).

3. Manufacture

3.1. Monomer Production. The key industrial monomer is 2,4,6-trimethyl-2,4,6-tris-(3,3,3-trifluoropropyl)cyclotrisiloxane [2374-14-3], which is produced by the hydrosilylation of 3,3,3-trifluoropropene [677-21-4] with methyldichlorosilane [75-54-7], catalyzed by various platinum and other noble metal compounds (eq. 3).

$$CF_3CH{=}CH_2 + CH_3{-}SiHCl_2 \longrightarrow CF_3CH_2CH_2Si(CH_3)Cl_2 \qquad (3)$$

The preparation of 3,3,3-trifluoropropene in high yield has been described (8). The hydrosilylation reaction can also be conducted using peroxides, radiation, or photochemical means. The hydrosilylation product, 3,3,3-trifluoropropylmethyldichlorosilane [675-62-7], is hydrolyzed with water to form a hydrolyzate siloxane mixture of cyclic siloxanes and linear hydroxyl end blocked siloxanes (eq. 4). This hydrolyzate mixture is washed to remove residual acid and then made basic with sodium hydroxide or potassium hydroxide. Distillation of the resulting mixture under reduced pressure affords the cyclotrisiloxane monomer as the lowest boiling siloxane. Base catalysis continues to rearrange both linear and cyclic materials in the distillation pot to re-form additional cyclotrisiloxane, which can then be recovered until nearly all the siloxane material is converted to useable cyclotrisiloxane unit monomer.



(4)

Preparation of other fluorosilicone monomers follows methods similar to that described above. For example, 2,4,6-trimethyl-2,4,6-tris(3,3,4,4,5,5,6,6,6-nona-fluorohexyl)cyclotrisiloxane [38521-58-3] is produced from 3,3,4,4,5,5,6,6,6-nona-fluorohexene [19430-93-4] and methyldichlorosilane in three steps (9).

3.2. Polymerization. Cyclotrisiloxanes are strained ring compounds. Polymerization is driven by relief of this ring strain. Acid- or base-catalyzed equilibration reactions of cyclotrisiloxane with a measured amount of end-blocking agent lead to fluid polymers with predictable molecular weight distributions. The amount of added end blocking agent controls polymer chain length. Various polar, aprotic solvents are known promoters, including tetrahydrofuran (THF), acetonitrile, and dimethylformamide (DMF). The reactions with metallic base catalysts (MB) adhere to the following order of decreasing rate: $K > Na > Li$. After neutralization or removal of the catalyst, fluid polymers are used as is or to formulated for specific applications. If a reactive end blocking group is incorporated during polymerization, the fluid polymer is then useful for making a coating, a sealant, or a liquid rubber product. Copolymers with other siloxanes can also be produced to give intermediate properties.

High molecular weight polymers or gums are made from cyclotrisiloxane monomer and base catalyst. To achieve a better curing gums, vinyl groups are added at 0.1–0.6% by copolymerization with methylvinylcyclosiloxanes. Gum polymers have a degree of polymerization (DP) of $\sim$5000 and are useful for the manufacture of fluorosilicone rubber. In order to achieve the gum state, the polymerization must be conducted in a kinetically controlled manner because of the rapid depolymerization rate of fluorosilicone. The expected thermodynamic end point of such a process is the conversion of cyclotrisiloxane to polymer and then rapid reversion of the polymer to cyclotetrasiloxane [429-67-4]. Careful control of the monomer purity, reaction time, reaction temperature, and method for quenching the base catalyst are essential for reliable gum production.

3.3. Formulations. Fluorosilicone rubber, greases, sealants, and coatings are typically filled systems. Additional materials are added including reinforcing fillers, extending fillers, pigments, thermal stabilizers, acid acceptors, handling additives, and/or conductive fillers. Channel sealants and greases are used as is after the addition of filler, whereas rubbers, curable sealants, and coatings need additional cure ingredients. Fluorosilicone bases are gums with pretreated or *in situ* treated fumed or precipitated silica fillers. Fluorosilicone compounds are readily available with peroxides or hydrosilation cure systems to produce various rubber products. These rubber products are based on high molecular weight ($M_w > 700{,}000$) polymers, but because of the freedom of rotation of the silicon–oxygen bond they are soft and easily processed in conventional mixers, water-cooled mills and calenders. Processing characteristics can be modified with hydroxy-containing low viscosity silicone oils, silicone gums, 1–10 parts of polydimethylsilicone softeners, 1–50 parts of fumed or precipitated silica fillers and optional extending fillers. Most fluorosilicone rubbers can also be colored by the addition of pigments.

3.4. Cure Chemistries. Fluorosilicones are available with appropriate reactive groups to be cured using typical silicone network chemistries such as peroxide cure, hydrosilation and condensation cure. Fluorosilicone elastomers can be peroxide-vulcanized by a free-radical mechanism using vinyl side groups that have been incorporated into the basic polymer structure during the initial polymerization process. Peroxide initiated cross-linking results in a carbon–carbon bond formed by the reaction of free radicals. The free radicals are generated in the polymer via the peroxide radicals, either by abstracting hydrogen from a methyl group or by adding to a vinyl group. During the vulcanization, the peroxide forms volatile by-products. Typical cure cycles are 3–10 min at 115–177°C, depending on the choice of peroxide. As with most fluoroelastomers, a postcure of 4–24 h at 150–200°C is recommended to maximize long-term aging properties. This postcure results in increased tensile strength, a higher cross-link density, and lower compression set.

Another form of cure is hydrosilation, the 'addition reaction' of one polymer containing a SiH functionality with a second polymer containing a vinyl functionality. These two polymers are made individually by copolymerization methods and then formulated prior to vulcanization into two-part or inhibited one-part systems. The vulcanization reaction is usually catalyzed by platinum compounds or other noble metal compounds. Heat may or may not be employed, depending on the catalyst or inhibitor selected. The resulting $-CH_2CH_2-$ linkage between siloxane chains vulcanizes the polymers into the desired elastomeric form. Many gels, sealants, rubbers, including liquid silicone rubber, (LSR) systems, use this type of vulcanization for a very clean and rapid cure cycle.

3.5. Rubber Fabrication. Fluorosilicone elastomers can be molded, extruded, or calendered by any of the conventional methods employed in the industry. Compression molding is the most widely used method and is ideal for a many fabrications at 115–170°C and 5.5–10.3 MPa (800–1500 psi). Injection molding becomes increasingly important for high production operations and generally requires higher temperatures and pressures than compression molding. Transfer-press molding is particularly useful for molding complex parts in a multicavity press. Where dimensional accuracy of molded parts is important, shrinkage of the parts must be considered in the design of the mold. Linear shrinkage of most fluorosilicones is 2.5–3.5%.

Standard rubber equipment may be used with fluorosilicone elastomers. Extrusion techniques are used to make tubes, rods, gaskets, preforms, etc. Calendering is used to produce long, thin sheets of fluorosilicone elastomers and to coat fluorosilicones on reinforcing substrates, eg, certain polymers and metals, to provide the protection of fluorosilicones at a minimal cost. When very thin films are desired or when the vulcanizing temperature of typical fluorosilicones is too high for the supporting substrate, room temperature vulcanizing (RTV) dispersions are commonly available. Dispersions of fluorosilicone gums, bases, and fully compounded stocks, with or without catalysts, can be used to make coatings for many fibrous metal or polymeric substrates. It is necessary to maintain dispersion neutrality to maximize the physical properties of the resulting coating. Usually a fluorosilicone primer is recommended for polymeric or metallic substrates for better bonding.

4. Economic Aspects

Globally, there are a small number of basic fluorosilicone producers. General Electric Co. and Dow Corning Corp. dominate in the United States and Europe, ShinEtsu in Japan. Production capacity is emerging in China and Russia (10). Prices tend to be ~\$50–55/kg and higher depending on the physical form and the application. In general, fluids are more expensive than elastomers. Not withstanding that, some specialty aerospace fluorosilicone elastomers exceed \$500/kg.

Production capacity of fluorosilicones is estimated at >6.0 thousand metric tons. The worldwide market for fluorosilicone elastomers was estimated at 2–3 thousand metric tons in 2002, with a \$100–150 million market value (2).

5. Health and Safety Factors

Information on fluorosilicone polymers is limited to safe handling information available in specific fluorosilicone product brochures and Safety Data Sheets. The only know hazard outlined in the MSDS is the evolution of toxic trifluoropropionaldehyde >150°C in air or an oxygen environment. Ventilation must be provided to control vapor exposure. Aerosol-spray applications may require added precautions especially those at high temperature in air.

No known chronic health effects have been reported. Eye contact with fluorosilicone fluid materials may cause temporary eye discomfort with redness and dryness similar to wind burn. A single prolonged skin exposure (24–48 h) causes no known adverse effect. Small amounts transferred to the mouth by the fingers during incidental use should not cause injury. Swallowing large amounts of the fluid may cause digestive discomfort. Attempted inhalation of fluids showed no eye or respiratory passage irritation. Fluorosilicone sealant and rubber materials use a variety of curing agents. Curing to the final form usually releases small amounts of volatile by-products and unnecessary exposure during curing should be avoided.

6. Uses

6.1. Surface Protection.

The surface properties of fluorosilicones have been studied over a number of years. The CF_3 group has the lowest known intermolecular force of polymer substituents. A study (4) of liquid and solid forms of fluorosilicones has included a comparison to fluorocarbon polymers. The low surface tensions for poly(3,3,3-trifluoropropyl)methylsiloxane and poly(3,3,4,4,5,5,6,6,6-nonafluorohexyl)methylsiloxane both resemble some of the lowest tensions for fluorocarbon polymers, eg, polytetrafluoroethylene.

Solutions of fluorosilicones impart oil and water repellent finishes to nylon–cotton fabrics. One series of C1 through C9 perfluoroalkyl substituents with varying structures were attached to silicon through amide or ether linkages. The fluorosilicones having perfluorinated straight-chain substituents with seven or more carbons gave the best repellencies (11) and exhibited durability toward repeated laundering, wear, and dry cleaning. The amide linkage to silicon was preferred over the ether linkage. Some nonfluorinated silicone can be tolerated in a fluorosilicone copolymer without affecting the repellency of the resulting treated fabric (see TEXTILES, TESTING).

6.2. Medical.

Fluorosilicones find multiple applications in medical treatment. Medical devices such as gastric feeding tubes use fluorosilicone rubber balloons for feeding tube retention while resisting gastric fluids. The low permeability of fluorosilicone versus dimethylsilicone is utilized to control the rate of release in drug devices and in medical tubing to stop the migration of active ingredients into the tubing. Fluorosilicone fluids are used in the treatment of detached retina and other eye diseases.

6.3. Personal Care.

Fluorosilicone fluids and copolymers (cross-polymers) as well as dimethylsilicone (dimethicone) are used in a variety of personal care applications. The oil resistance imparted by the fluorine combined with the water resistance and feel of silicone provide durability and ease of application to cosmetic foundations. The low permeation of fluorosilicone provides a degree of protection as a hand lotion.

6.4. Foam Control.

Fluorosilicone fluids and copolymers are effective antifoams in nonaqueous systems. Successful application in the petroleum industry allows the full capacity of gas–oil separators to be used on offshore production platforms. Diesel fuels also require fluorosilicone antiforms due to the profoaming nature of dimethylsilicones in nonaqueous systems (12). Fluorosilicone antifoams do not typically require additional silica for performance (Defoamers).

6.5. Lubrication.

Fluorosilicone fluid polymers or oils are used as lubricants for pumps and compressors in harsh chemical service, such as those using acids, bases, and halogenated compounds and solvents. Fluorosilicone greases are found in bearing lubrication applications that require high and low temperature performance. Fluorosilicone fluids and greases resist oxidative degradation which can form deposits, while providing a flatter viscosity–temperature profile than the hydrocarbon oils. They are chemically inert, resist wash out from fuels and solvents and do not corrode or react with most engineering materials of construction, including many metals, rubbers, and plastics. A serviceable temperature range is −40 to 204°C in open systems and up to 288°C in closed systems. The high autoignition temperature (>480°C) makes air service possible over a wider temperature range with fire-resistant properties.

6.6. Encapsulants. Fluorosilicone fluids and copolymers with vinyl functionality can be cured using the platinum catalysted hydrosilation reactions. The cure can be controlled such that a gel or a soft, clear, jelly-like form is achieved. Gels with low (12% after 7 days) swell in gasoline fuel are useful (9) to protect electronics or connectors from dust, dirt, fuels, and solvents in both hot (up to 150°C) and cold (down to −65°C) environments. Both potting materials with *in situ* cure and applied tape can be used as fabrication methods. Applications include connector seals, sensor potting, and dielectric gels for automotive, aerospace, and electronic industries where harsh fuel–solvent conditions exist while performance requirements remain high (13).

6.7. Sealants. Sealants are available in three different conventional forms: one-part moisture cure, two-part systems and noncuring sealants. Moisture cure sealants are available in acetoxy or methoxy cure systems. Two-part systems are typically hydrosilation cure systems. Two-part sealants are primarily used where thick section cure is required. Noncuring sealants are used as fillets, faying surface seals, and channel sealants. They supply a flexible seal in joints exposed to fuel.

Uses include both subsonic and supersonic aircraft fuel sealing applications, where temperatures of −57 to 232°C are experienced while in constant contact with aircraft fuel. Filleting sealants for integral fuel tanks built into the aircraft wings and noncurable channeling sealants comprise their primary uses. They are also used in bonding, sealing, caulking, encapsulating, and potting applications (14).

6.8. Rubber. The majority of fluorosilicone is used in elastomers. Fluorosilicone elastomers can be formulated to provide specific durometer (hardness), tear strength, modulus, and solvent resistance properties. The specific gravity is 1.35–1.65. Shore A Durometer ranges from 20 to 80. High tear materials are designed to resist tearing 52.5 kN/m (300 ppi). Modulus at 100% elongation can range from 0.4 to 6.2 MPa (60 to 900 psi). Elongation is 150–700%. Compression set can be as low as 6% (22 h/177°C). Tensile strength is 5.5–12.4 MPa (800–1800 psi). Rubber resiliency (Bashore) is 14–30%.

Fluorosilicone rubber is used as O-rings for fuel lines containing gasoline and aviation fuels (15). Often fuel lines use both fluorosilicone and fluorocarbon elastomer O-rings; the former for low temperature sealing and the latter for reduced permeation of fuels. Most O-rings and gaskets have a compression between 15 and 25%. A recent paper studied compressed permeation of CE10 for O-rings and gaskets (16). Typically an 80% reduction from flat sheat permeation is seen with O-rings at 20% compression in ASTM Fuel C with 10% ethanol. The compressed reduction in permeation is a result of the flexibility of the siloxane backbone. The free volume is compressed and filled by other atoms within the polymer. Lower permeation is then a result of compression and usually approaches the permeation of fluorocarbon elastomers (FKM) polymers. Active control of emissions is achieved through the use of fluorosilicone diaphrams, for example: natural vacuum leak detection systems and charcoal canister vapor control. Other important applications are the antiflowback valve used to prevent fuel excape in the event of a vehicle roll over, fuel line check valves, and pulsation dampners in fuel rails. Extreme conditions under the hood in modern trucks and automobiles has also lead to the use of fluorosilicones as inner liners for oil resistant laminated tubing and hoses (17) with this material such as turbo charger hose liners.

Hydraulic fluid resistance makes fluorosilicones the choice for the manufacture of the flexible bellows (18) between the hydraulic fluid reservoir and the suction pump on aircraft. Its use allows for fluid continuity during normal and inverted flight attitudes in military aircraft. Resiliency provides another opportunity for the rubber functioning as a cushion between stainless steel loop clamps and fuel–hydraulic fluid lines in aircraft. Use in jet engines (19) provides vibration damping, which prevents the clamp abraiding the tube surfaces in normal service as well as at temperatures down to -55°C.

Electrically conductive rubber (20) can be achieved by incorporation of conductive fillers, eg, use of carbon or metal powders. These rubbers exhibit volume resistivities as low as $10^{-4}\Omega\cdot$ cm. Applications include use in dissipation of static charge and in conductive bridging between dissimilar electronic materials under harsh operating conditions.

At elevated temperatures fluorosilicones retain a greater percentage of their initial properties than organic rubbers such as FKM (6). Fluorosilicones tested for abrasion resistance using the Tabor abrasion method have been found to be more resistant to abrasion than fluorocarbon rubber (21). Abrasion resistance combined with low swell in lubricating oils and greases allows the use of fluorosilicone rubber in rotating and sliding seal applications that must function at both low and high temperature.

Mechanical blends of fluorosilicone elastomers and fluorocarbon elastomers are well known. Blends are used to create O-rings and gaskets having good low temperature sealing properties due to the flexibility of the fluorosilicone in the blend matrix. The blends also have reasonable permeation results both in compressed and tube liner results (22). Methods of compatibilization (23) have been attempted but most blends remain simply mechanical blends. Fluorosilicone elastomers can also be alloyed with FKM. Resulting alloys combine high chemical resistance of FKM with low temperature performance of fluorosilicone elastomers (24).

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Table 1. **Bond Lengths and Angles**[a]

	Bond length, Å	Bond angles, °
F–C–F	1.30–1.32	108
C–C–C	1.54	112
H–C–H	1.09	109
C–Si–C	1.88–1.90	109
Si–O–Si	1.63–1.65	130

[a] See Ref. 3.