Silicones, particularly silicone rubbers, have found use in a wide variety of transportation applications.

Nonreinforced cross-linked silicone polymer networks are very weak. However, when filled with precipitated or fume silica reinforcing fillers and compounded into silicone elastomers or silicone rubbers, a tremendous improvement in mechanical properties is seen. Specific silicone rubbers have tear strengths of 60 kN/m and tensile strengths above 10 MPa, yet with low relative density, making them cost attractive on a volume basis (see Table 1) [1].

Table 1. Typical Mechanical Properties of Selected Rubber Families

<table>
<thead>
<tr>
<th>Material</th>
<th>Unit</th>
<th>Silicone</th>
<th>Natural Rubber</th>
<th>EPDM</th>
<th>Neoprene</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tensile strength</td>
<td>MPa</td>
<td>4 - 12</td>
<td>28</td>
<td>24</td>
<td>28</td>
</tr>
<tr>
<td></td>
<td>psi</td>
<td>990 - 1265</td>
<td>4000</td>
<td>3500</td>
<td>4000</td>
</tr>
<tr>
<td>Elongation at break</td>
<td>%</td>
<td>570 – 1000</td>
<td>700</td>
<td>550</td>
<td>500</td>
</tr>
<tr>
<td>Hardness range</td>
<td>Shore A</td>
<td>20–90</td>
<td>30-90</td>
<td>25-85</td>
<td>35-90</td>
</tr>
<tr>
<td>Min. operating temperature</td>
<td>oC</td>
<td>-60 (*)</td>
<td>-60</td>
<td>-50</td>
<td>-40</td>
</tr>
<tr>
<td>Max. operating temperature (continuous)</td>
<td>oC</td>
<td>230</td>
<td>100</td>
<td>140</td>
<td>100</td>
</tr>
<tr>
<td>Relative density</td>
<td></td>
<td>1.15</td>
<td>0.92</td>
<td>0.86</td>
<td>1.23</td>
</tr>
</tbody>
</table>

(*) Special grades down to -116 ºC

Adding high surface area fillers, such as silica, increases the viscosity of the blend and so requires the use of silica surface treatment agents to maintain enough ease of processing and prevent crepe hardening.

Apart from reinforcing silica, other ingredients are included in the formulation, such as peroxide or cross-linkers and catalyst. These provide a “cure package” to cross-link the silicone polymer chains into a silicone rubber, as silicone rubbers are thermosets and are “cured” at elevated temperatures.

Silicone rubber compounds are typically delivered as one-part materials to be crosslinked at elevated temperatures by either peroxide- or platinum-based catalysts. Where a one-part platinum catalyst based material is used, the activity of the platinum catalyst at room temperature has been reduced using appropriate inhibitors. These one-part products do not require mixing prior to use but have limited shelf life, typically ranging from three to six months. To ensure sufficient shelf life, a platinum catalyst encapsulated in a thermoplastic resin can be used, where upon heating, the capsule melts and liberates the platinum catalyst [2].

The cross-linking densities in silicone rubbers are low and as the cure package has no detrimental effects upon the polymers, silicone rubbers retain most of the key properties of the silicone polymers from which they are made. They offer resistance to weathering, ozone and UV radiation, and aesthetically they are transparent and therefore easy to pigment. Glass transition temperature remains low, meaning that these silicone rubbers can be used in
regions that encounter extremes of cold. Conversely, their stability at very high temperatures means they can survive the harshness of modern engine compartments, where rubbers are expected to coexist next to hot metal components, and where upper service temperatures have been steadily increasing due to the higher running temperatures demanded by more efficient engines.

Silicone rubbers are easy to process and various types are available. Liquid silicone rubbers (LSRs) are paste-like materials and are widely used in injection molding for flashless parts, fabric coating, dipping and extrusion coating processes. High consistency rubbers (HCRs) and fluorosilicone rubbers (FSRs) are gum-like materials and can be calendered; injection, compression or transfer molded; or extruded.

Grades of silicone rubbers can be formulated to resist attack from organic oils and greases. Where increased resistance to organic fuels is required, fluorosilicone rubbers (in which some of the -CH₃ groups along the siloxane backbone have been replaced by -CH₂CH₂-CF₃ groups) offer a step change in fluid resistance (see Table 2) [1]. This is a result of the slight polarity and the sheer size and bulkiness of the trifluoropropyl group, which imparts significant steric hindrance to the molecule and also reduces the free volume of the network. These factors combine to severely limit the penetration and swelling of the FSR by many solvents.

Table 2. Fluid Resistance of Standard and Fluorosilicone Rubbers

<table>
<thead>
<tr>
<th>Rubber Type</th>
<th>Water 3 days / 100 °C</th>
<th>ASTM Oil #3 3 days / 150 °C</th>
<th>Toluene 7 days / 24 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Delta duro % swell</td>
<td>Delta duro % swell</td>
<td>Delta duro % swell</td>
</tr>
<tr>
<td>MQ</td>
<td>-5</td>
<td>+5</td>
<td>-25</td>
</tr>
<tr>
<td>VMQ</td>
<td>-5</td>
<td>0</td>
<td>-20</td>
</tr>
<tr>
<td>FVMQ</td>
<td>0</td>
<td>0</td>
<td>-5</td>
</tr>
</tbody>
</table>

(*) na: not available.

Note: MQ: dimethyl silicone based rubber
VMQ: vinyl methyl silicone based rubber (HCR)
FVMQ: fluoro vinyl methyl silicone based rubber (FSR)

Using silicones in the automotive industries is not without controversy. In the trade, there are many stories about paint shop managers banning silicones from their production areas. The issue here is surface contamination from either liquid silicones or from low molecular weight “airborne” volatile siloxanes liberated from other silicone-based compounds used in the vicinity. All are capable of binding to surfaces to be painted, leading to poor paint wetting and disastrous “orange peel” problems. This is linked to the low critical surface tension of wetting they induce after adsorption. This is a problem that can be prevented by using simple good working practices.

Another issue is headlight “fogging” linked to the degradation of low molecular weight volatile species and deposition on headlight lenses sealed to their frames with silicone sealants. These issues are real and need adequate management, but with appropriate precautions even silicone fluids are currently used in many automotive applications. For example, silicone polyethers are used as profoamers in the PU foams present in many cars, sometimes unknown to the production engineers, and silicone fluids are used in viscous couplings. In both these applications silicone use is without problems. On average, a car
contains approximately 3 kg of silicones, mainly silicone rubbers, which are used to produce many parts.

**Body Components**
- Heater hose
- Oil seal, water seal, air seal - filler cap O-ring seal
- Vibration and sound damping material; rubber exhaust/muffler hanger
- Mirror mount adhesive

**Chassis**
- Heater hose – brake hose and clutch hose
- Oil seal, water seal, air seal – dust cover seal, CVJ boot, and brake cap seal
- Dynamic seal – power steering oil seal and booster piston seal
- Vibration/sound damping material – engine mount and suspension bushing

**Electrical Components**
- Spark plug boot
- Ignition cable
- Lamp cap - headlamp and fog light
- Weather pack connector seal

**Fuel Systems**
- Fuel seal – fuel filler seal, quick connector seal
- Diaphragm

**Power train**
- Turbocharger hose and heater hose - turbocharger hose, emission control hose, air duct hose, long life coolant hose (LLC)
- Oil seal, water seal, air seal – gasket material for intake manifold gaskets, oil pan gaskets, rocker cover gaskets, front cover gaskets, radiator tank gaskets, oil filters, O-ring in long life coolant (LLC)
- Dynamic seal – crank shaft seal, camshaft seal, transmission oil seal

**Safety**
- Air bag coatings

Specific examples related to land transportation and aviation are described below.

**Land Transportation**
*Turbocharger Hoses.* Turbocharger hoses, also known as intercooler or crossover hoses, connect the turbocharger outlet to the air intake of the engine. These hoses are reinforced with fabrics such as knitted polyester, woven Nomex® or woven glass fibers to withstand high operating pressures during use. Stainless steel rings may also be used to limit the extent of hose expansion under pressure. In this application, a thin, single layer of FSR is typically used as the hose inner lining to prevent the leaking of engine lubricants, which condense onto the inside of the hose when the engine cools. The inner layer of FSR is covered with a number of plies of HCR to give added strength and increased heat resistance. Such FSR/HCR combinations are particularly suitable for turbocharger hoses.
Water Coolant Hoses. Silicone coolant hoses are used to carry water, air and oil, while resisting high temperatures and degradation. The increasing use of long-life coolants and aggressive rust inhibitors using organic acid technology (OAT) in combination with complex engine design makes hose replacement time consuming and expensive. Therefore, engine designers are looking for a material that is “fit and forget.” The lifetime cost of a silicone hose, when taken in conjunction with service intervals and replacements, often offers a cost saving over alternative materials that are perceived as lower cost.

Air Bags. Rapid growth in the use of automotive air bags has resulted in a corresponding growth in the use of silicone for this application. Air bags are now commonplace in most cars, from luxury to entry models. The initial driver’s air bag also has been supplemented with passenger and side-curtain air bags to protect occupants in the event of a roll. Each bag has its specific requirements, whether initial impact softening through rapid inflation followed by controlled deflation, or sustained retention of pressure for protection when a car repeatedly rolls over. The excellent aging properties of silicone rubber means that an air bag that has remained folded into a small volume for many years functions perfectly when required, expanding to hold a high temperature gas as it explodes into action.

Anti-Drain Back Valves. This application requires grades of silicone rubber that can resist degradation from engine oil. Such valves made of silicone prevent engine lubricant from draining into the bottom of the sump and ensure the engine is properly lubricated upon start-up. Specific grades of silicone can resist the chemical attack of engine lubricants and remain flexible at extremely low temperatures, while at the same time offering extended product life.

Flexible Connections in Trains and Buses. The flexible gangway connections between bus and train carriages have been made with a number of differing materials, but an ethylene acrylic elastomer was the most popular choice for a time, mainly based on cost. However, after a number of high profile fires and many fatalities, designers and specification writers reviewed the requirements for a material to fulfill this application. They considered features such as long service life, environmental resistance to cracking and fading, retained flexibility in regions with very cold winters, abrasion resistance, resistance to burning and, when fire does catch hold, low smoke and low toxicity (LSLT) properties, combined with ease of fabrication for companies already using the ethylene acrylic elastomer. Low smoke density and low smoke toxicity is particularly important in underground trains circulating in low diameter tunnels, as the only escape route in case of fire is through the carriage ends. Silicone became an obvious choice, offering a step change in LSLT performance and meeting the BS 6853:1999 category 1a standard.

Aviation
Many features that make silicone an ideal material for automotive applications also hold true for applications in aviation. The retained flexibility of silicone at the low temperatures found at high altitude, the resistance to burning and the subsequent LSLT properties are crucial. Combined with fabricators’ ability to construct complex parts with a material that is safe and easy to handle (thus contributing to cost effectiveness of the finished part), these characteristics make silicone a frequently used material in the world of aerospace. Applications include door and window seals, aileron flap seals and safety devices that require
short term resistance to very high temperatures in the event of a fire. In areas that require resistance to jet fuel and lubricants, FSR can be used for hydraulic line and cable clamp blocks, fuel control diaphragms and fuel system O-rings. Silicone rubber products can withstand tremendous stresses and temperature extremes – whether in the air, the stratosphere or the frozen vacuum of space.
References


This article has been published in the chapter “Silicones in Industrial Applications” in Inorganic Polymers, an advanced research book by Nova Science Publishers (www.novapublishers.com); edited by Roger De Jaeger (Lab. de Spechtrochimie Infrarouge et Raman, Univ. des Sciences and Tecn. de Lille, France) and Mario Gleria (Inst. di Scienze e Tecn. Molecolari, Univ. di Padoa, Italy). Reproduced here with the permission of the publisher.