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Food Grade Silicone Braided Hose

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Abstract

Silicone elastomers are becoming more and more prevalent for Food Industry. This is because with the fact that the curing systems of organic elastomers often include amines and other additives leading to potential toxic contaminants, such as nitrosamines. On the other hand there are silicone rubbers/elastomers which are amine free and, in most cases, are platinum cured. Such curing systems allow for biocompatibility. Correctly processed parts do not show detectable nitrosamine levels without and after proper post cure. Other favorable properties of silicone elastomers for food contact are sterilisability, steam, heat and chemical resistance. Unlike most organic elastomers, silicone will not only form such harmless combustion products, it will also produce very little smoke and, hence, permit a good degree of visibility in the event of a fire. Further, silicones are capable of forming a stable ash, which in extreme cases will turn into very hard ceramic. Silicone hose has excellent performance characteristics at extreme high and low temperatures. The guide explains the basic manufacturing process that I hope will bring a greater appreciation for the hard work involved in manufacturing high performance silicone hose.

1. Introduction

Silicones are suitable for use in contact with food. This is, indeed, true. The reasons are in the compatibility of silicones with their environment, chemical resistance, physical and mechanical properties.

Silicone elastomers are used in many different areas ranging from packaging aids or elements to tubings for the food industry. Silicone elastomers in contact with foodstuffs have to comply with relevant legislation and regulations.

Perhaps the most famous regulations in that respect are the German BgVV Recommendation XV 'Silicones' and the US Food and Drug Administration (FDA) Regulation CFR21 Section 177.2600. These contain positive lists of sanctioned ingredients for rubber parts in contact with food. What is not listed must not be contained in the silicone elastomer formulation. BgVV also regulates the amount of volatile matter in the silicone elastomer. The weight loss of a silicone part must not exceed 0.5% after heat treatment for 4 hours at 200 °C. Further, the two regulations prescribe acceptable levels of extractables, etc.

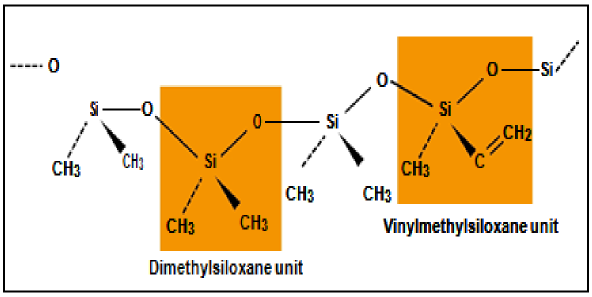

Figure 1. Repeat unit of silicone Rubber

Here's the list of silicones mentioned from FDA CFR 177.2600 section (c,4,i): Silicone (Si) elastomers containing methyl groups, Silicone (Psi) elastomers containing methyl and phenyl groups, Silicone (Vsi) elastomers containing methyl and vinyl groups, Silicone (Fsi) elastomers containing methyl and fluorine groups, Silicone (PVsi) elastomers containing phenyl, methyl, and vinyl groups.

Silicone elastomers meet such requirements, if they are processed correctly and have undergone sufficient post cure. Post curing is used in order to finalize vulcanization and strip off volatiles which are contained in the rubbers as cured.

2. Silicone

Silicone rubber is an elastomer (rubber-like material) composed of silicone—itself a polymer—containing silicon together with carbon, hydrogen, and oxygen. Silicone rubbers are widely used in industry, and there are multiple formulations. Silicone rubbers are often one- or two-part polymers, and may contain fillers to improve properties or reduce cost. Silicone rubber is generally non-reactive, stable, and resistant to extreme environments and temperatures from −55 °C to +300 °C while still maintaining its useful properties. Due to these properties and its ease of manufacturing and shaping, silicone rubber can be found in a wide variety of products implants.

Table 1. Mechanical properties

Hardness, shore A	10-90
Tensile strength	11 N/mm ^{2}
Elongation at break	100-1100%
Maximum temperature	+300 °C
Minimum temperature	-120 °C

Table 2. Summary of physical properties at room temperature for silicone

Durometer Hardness, Shore A:	25-30
Tensile Strength, Psi:	Up to 1600
Elongation, %	Up to 700
Tear Resistance, Lb/In	Up to 250
Compression Set, %:	Down to 5

During manufacture, heat may be required to vulcanize (set or cure) the silicone into its rubber-like form. This is normally carried out in a two stage process at the point of manufacture into the desired shape, and then in a prolonged post-cure process. It can also be injection molded.

Table 3. Silicone polymer classifications ASTM D-141

Classification	Description
MQ	Dimethyl Silicone General Purpose, Sponge
PMQ	Methyl Phenyl Silicone Low Temperature
VMQ	Methyl Vinyl Silicone Low Compression Set
FVMQ	Fluorosilicone Solvent Resistence

2.1. Major classes

Silicone rubbers are essentially divided into two groups of materials, i.e., room temperature vulcanizing (RTV) and high temperature vulcanizing (HTV). RTV systems are able to cure at room temperature and HTV systems at temperatures well above 100 °C. A number in the name indicates the number of components that upon mixing will form a curable composition, e.g., RTV-2.

HTV rubbers are mainly so-called solid silicone rubbers. They have a very high viscosity in the uncured state and appear as solids. This behavior has also led to the creation of the term 'High Consistency Rubber' (HCR).

Approximately 25 years ago a new group of materials appeared that was intended for processing in injection moulding machines. Because of their low viscosity and paste-like behavior they were named liquid silicone rubbers (LSR) or simply liquid rubbers (LR). It is common to use LSR or LR as an abbreviation instead of HTV, even though they vulcanize at high temperatures as in the case of solid silicone rubbers.

For the most part all LR materials are 2 component systems which cure after mixing and at elevated temperatures.

In summary the silicone industry uses the terms RTV- 1, RTV-2, LR or LSR, HTV or HCR.

Table 4. Qualitative comparison between some commonly used elastomers

	Fully Automatic Production	**Waste Free Production**	**Chemical Resistance**	**Cold Flexibility < -40°C**	**Heat Stable > 200°C**	**Pigmentable Any Color**
TPE	++	++	+/-	-	-	+
EPDM	+	-	+/-	-	-	-
Natural Rubber	-	-	-	-	-	-
Polyureth -ane	+	+	+	-	-	++
Silicone	++	++	+	++	++	++

Note: ++ Very Good , + Good , -Poor

Food & Beverage Hose: this silicone hose is made with platinum cured silicone and is produced in a clean room. The silicone normally meets USP CLASS VI requirements as do the stainless fittings for the hose. Platinum cure silicone will not impart a taste or odour to critical streams. The hose use may include; pharmaceutical, biomedical, cosmetic, and food & beverage applications. It is often made as 3 or 4-ply with or without convolutions and stainless steel wire reinforcement. This hose, (same as all silicone hose) is not recommended for continuous steam applications. The general temperature range is -65°F to 500°F when reinforced with Nomex®.

Consider these performance factors;

- Resistance to temperature extremes -65°F -350°F and even up to 500°F.
- Long service life compared to EPDM and organic materials.
- Weather resistant to harsh sunlight & dry conditions, ozone, and rain water.
- High resistance to water absorption.
- Odourless and tasteless, inert.
- Resistance to compression set & deformation, esp. at high & low temps.
- No out-gasing since it doesn't contain sulfur or acid producing chemicals.
- Will not cause staining, corrosion, & won't support mold or bacteria growth.
- Offered in attractive color options and with a glossy or matte finis
- Cost effective, complex shapes can replace expensive metal tubes.
- Excellent physical properties; good burst strength, vacuum and kink resistance.
- Cost effective compared to metal tubes, a single hose eliminates multiple parts.
- Complex shapes are possible with offsets, spigots, multiple diameters, etc.

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3. Manufacturing process of silicone braided hose

A hose is a reinforced, flexible conduit used to move materials from one point to another or to transmit energy. It is flexible to accommodate motion, alignment, vibration, thermal expansion and contraction, portability, ease of routing, and ease of installation.

Most hoses are made up of three elements: (1) a tube, (2) reinforcement, and (3) an outer cover. The process begins with the reduction of silica (sand) to elemental silicon metal which is then mechanically ground and reacted with methyl chloride at 300ºC in the presence of a copper catalyst.

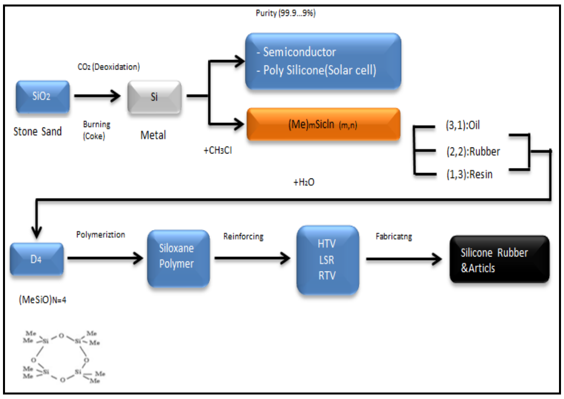

Figure 2. Schematic of the production of silicone elastomers

This results in the formation of reactive methylchloro silanes which are fractionally distilled and separated into their mono, di, and tri counterparts. Note that the dichloro species is most important for forming long linear polymer chains since its bifunctionality allows it to "grow" chemically in two dimensions. The tri-chloro species forms three dimensional crosslink networks and, although important for rigid, nonelastomeric molding resins, must be separated from the di stream to avoid gelling the polymer.

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After distillation, the dimethyldechlorosilanes are hydrolyzed to form silanols which rapidly condense to cyclic siloxanes and low molecular weight linear siloxanes. The latter are reacted with caustic to produce cyclic siloxanes, specifically dimethyl tetramer or D4 which is the primary input for all dimethyl silicone rubber polymer and which is a clear, low viscosity liquid. Ring opening polymerization of the cyclic D4 is then accomplished via strong base resulting in linear polymer whose molecular weight (viscosity) is controlled by the addition of monofunctional siloxanes which function as chain stoppers.

3.1. Silicone rubber compounding

Unlike organic polymers, silicone polymer by itself is relatively weak and produces tensile strengths of only 1.0 Mpa when crosslinked. To achieve useful engineering properties, it is necessary to reinforce the polymer by the addition of very fine, high surface fillers which are compatible chemically with the silicone polymer

3.2. Fillers

The most common reinforcing filler used in silicone rubber compounds is fumed silica. Cross-linked silicone rubber compounds containing fumed silica typically have tensile strengths in excess of 10 Mpa, i.e., a factor of ten higher than the pure polymer.

Table 5. Formulation ingredients for silicone rubber compounds and their primary function

Component	Primary Function
Silicone Polymer	Inherent Chemical Properties
Reinforcing Filler	Physical and Rheological Properties
Extender Filler	Cost Reduction and Oil Resistance
Process Aid	Processability and Shelf Life Stability
Organic Peroxide	Crosslinking Agent
Metallic Oxide	Oil and Reversion Resistance
Platinum Complex	Addition Cure Catalyst and/or Flame Retardant
Iron Oxide, Titania	High Temperature Heat Stability
Phenyl Silicone Fluid	Self-Bleed or Self Lubrication
Teflon Powder	Increase Green Strength

Table 6. Fillers suitable for use with silicone polymers

Type	Reinforcement	Sp. Gravity	Particle dia. (millimicrone)	Surface area (m^2/gm)	1 Duro Pt. loading(pph)
Fumed silica	High	2.20	17 10	200 325	1-1.5 , 0.5-1.0
Precipit-ated Silica	High	2.00	22	160	1-1.5
Diatoma -ceous	Semi	2.15 -	3000	5	2.0

Earth		2.30			
Ground Quartz	Low	2.65	5000-30,000	--	3.0-5.0
Red Iron Oxide	Low	4.95	1000	--	--
Titania	Semi	3.90	300	9	--

3.3. Process aids

Process aids, also known as softeners, are reactive silicone fluids which chemically modify the surface of the silica fillers to reduce their association with the silicone polymer. Most process aids are liquids which can either be pre-reacted with the silica filler in a pre-treatment process, or can be introduced during the compounding/mixing phase to effect "in-situ" treatment. In many cases, both techniques are employed.

3.4. Vulcanization/curing of silicone rubber

There are two types of silicone curing one is peroxide and another one is platinum addition cure. The peroxide of choice for extrusion, and to minimize air inhibition, is bis (2,4- dichlorobenzoyl) peroxide. But, this peroxide gives rise to the formation of by products such as 2,4-dichlorobenzoic acid10 or various polychlorobiphenyl congeners (PCBs).These by-products can affect the stability of the tubing, diffuse and concentrate at the surface or "bloom" and/or lead to toxicological concerns.so it is desirable to use platinum addition cure for food grade hose.

3.5. Platinum-catalyzed addition cure

An alternative method for curing silicone rubber utilizes a silicone hydride (SiH) crosslinking agent in conjunction with methylvinyl silicone polymer. In the presence of a precious metal catalyst such as platinum, a true addition reaction occurs resulting in a uniformly vulcanized rubber without curative by-products. Since this reaction proceeds quite actively at room temperature, inhibitors play a crucial role in assuring adequate mixed shelf life and cure rate control at fabrication temperatures.
Addition cured materials are able to achieve extremely high levels of tear strength (50 – 60 KN/m) as a result.

Table 7. Peroxide cure vs addition cure

	Peroxide Cure	**Addition Cure**
Tight Surface		x
Low Surface Tack		x
Hot Air Cure	DCBP Only	x
Low Coefficient of Friction		x
Best Hot Tear Strength		x
Low Compression Set	x	
Optimum High Temperature	x	
Fast Cure Rate		x
Long Shelf Life	x	
Non-Blooming Extrusion		x
No Decomposition By-products		x
Lower Cost	x	
Easy Flash Removal		x
Catalyst Sensitivity		x
Potential Cure Inhibition		x

3.6. The Compounding Process

Silicone rubbers are most commonly mixed in an internal mixer such as a dough mixer or Banbury type mixer which provides additional shear through action of the ram. Pre-treated filler and devolatilized polymer allows the use of a "cold mix" to similarly achieve stable properties and is generally a more cost effective process.

3.7. Freshening and Milling

Freshening is the process of mechanically plasticizing or softening a rubber compound to develop consistency in fabrication. Silicone compounds are easily freshened on a two roll rubber mill equipped with a scraper blade on the fast roll to facilitate stock removal. A speed ratio on the rolls of 1.2 – 1.4 to 1 is required to shear the rubber as it passes through the nip which helps to promote good dispersion.

Milling is also utilized to add minor ingredients such as pigment and catalyst to the compound as it provides temperature control to prevent premature volatilization or decomposition of the catalyst.

3.8. Extrusion of silicone rubber

There are three basic methods of making hose have evolved: (1) non-mandrel, (2) flexible mandrel, and (3) rigid mandrel. In methods (2) and (3), the mandrels are used for support and as dimensional control devices for the hose tube during processing. Then after the hose building and, if necessary, the vulcanization are complete, the mandrels are removed, inspected and recycled.
Silicone rubber should be extruded at room temperature. In fact, it should not be allowed to reach a temperature above 54°C during extrusion, since higher temperatures may produce scorching and loss of vulcanizing agent.

Silicone tubing is made by extrusion of the above compounded elastomers, known as high consistency silicone rubbers (HCR). Typically, the screw should have a compression ratio in the range of 2:1 to 4:1 and an L/D (length/diameter) ratio of 8:1 to 12:1.

Deep flights in the feed section facilitate feeding of the compound. Stainless steel screens of 40 to 150 mesh are recommended to remove contamination, increase back pressure, reduce porosity, and provide better dimensional control. Silicone tubing is highly flexible and expands with increased intraluminal pressure.

3.9. Reinforcement

Reinforcement can be textile, plastic, or metal, alone or in combination, built into the body of the hose to withstand internal pressures, external forces, or a combination of both. The type and amount of reinforcing material used depends on the method of manufacture and on the service requirements.

In most cases it is located between the tube and cover. Occasionally there are hose applications not requiring a cover, in which case the reinforcement also acts as the outer protective layer.

When multiple plies of reinforcement are required to meet working pressure performance levels, typically they are applied one over the other normally separated with a rubber layer (friction or jacket) to fill voids, prevent adjacent reinforcement abrasion, and to maintain adequate hose component adhesion levels. Multiple plies may be applied individually or in a single pass through a multiple deck unit. Hose reinforcements are either textile, both synthetic polymeric and natural, or wire. Typical Fabric Reinforcement Silicon Hose is given below.

Temperature Range
Polyester -65° to 350°
Fiberglass -65° to 500°
Nomex® -65° to 500°
Meta-Aramid -65° to 500°

Reinforcing wire is used in a wide variety of hydraulic and industrial hose, primarily where textiles alone do not satisfy the special engineering requirements or the service conditions for which the hose is designed. For food grade hose SS316 wire can be used. Steel wire has strength, high modulus for dimensional stability, fatigue resistance, and low cost, and is the major reinforcement used in high pressure hose and in most suction hose.

Methods of applying these reinforcements are braid, spiral, knit, wrap, and woven. Selection of reinforcing equipment is dependent on pressure rating, size, fitting requirements, flexibility, and crush resistance levels. Braiding is probably the most common and traditional method of reinforcing hose. Braiders are described as vertical or horizontal depending on the direction the tube progresses through the machine during braiding. The two major classifications of braiders are tubular or “maypole” type and rotary type.

3.10. Cover

The cover is the outer element and can be made Blue, Red, or Black and is the last ply.

3.11. Cure / Vulcanize

There are a number of different methods to cure silicone material such as autoclave which provides heat & steam under pressure. The key is to achieve the proper temperature for the proper duration. The typical curing time is 30 min. or less and an approx. 300°F temperature.

3.12. Trimming

After the part is cured there is still a fair amount of work to do since the hose must be trimmed properly and as specified. Some parts require complex trimming with special notches, angles, and lengths.

3.13. Marking and packaging

A number of silicone parts require the hose to be marked and packaged in a specific way, very detailed marking and packaging requirements that use additional labour and materials will increase cost.

3.15. Cleaning and final inspection

The hoses are cleaned by hand with a cloth and the final inspection is completed in accordance with written criteria.

Summary

Silicone rubbers are often one- or two-part polymers, and may contain fillers to improve properties or reduce cost. Silicone rubber is generally non-reactive, stable, and resistant to extreme environments and temperatures from −55 °C to +300 °C. The siloxane bonds (–Si–O–Si–) that form the backbone of silicone (dimethyl polysiloxane) are highly stable. At 433 kJ/mol, their binding energy is higher than that of carbon bonds (C–C), at 355 kJ/mol. Thus, compared to common organic polymers, silicone rubbers have higher heat resistance and chemical stability, Flame retardency. At the extreme temperatures, the tensile strength, elongation, tear strength and compression set can be far superior to conventional rubbers although still low relative to other materials. Organic rubber has a carbon to carbon backbone which can leave them susceptible to ozone, UV, heat and other ageing factors that silicone rubber can withstand well. This makes it one of the elastomers of choice in many extreme environments, and so the hose made by silicone has very good properties to transfer food materials. It has a good elasticity and higher bending radius and higher flexibility with braiding technology. There’s a minimum bursting possibilities too.

Table 8. Tensile strength, elongation at break and tear resistance of a HTV silicone rubber at various temperatures

Temperature (^{O}C)	Hardness, Shore A	Tensile strength (N/mm^2)	Elongation at break (%)	Tear resistance (N/mm)
200	50	3.3	370	6.7
150	50	5.1	450	8.4

70	50	8.0	630	14.0
23	50	10.3	800	18.4
0	51	11.3	870	24.4
-40	53	14.8	910	39.8

Compared to organic rubbers, however, silicone rubber has a very low tensile strength. But the addition of Fumed silica as a filler can increase tensile strength and reduce the cost of material. The material is also very sensitive to fatigue from cyclic loading. Silicone rubber is a highly inert material and does not react with most chemicals. Curing agents used in other elastomers contain amine, chlorine that can affect the stability of the hose, diffuse and concentrate at the surface or "bloom" and/or lead to toxicological concerns, where the platinum used in silicone as a curing agent has no any toxicological effect. Due to its inertness, it is used in many medical applications and in medical implants. This advantage can be used in Food Industry too.

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