

Silicones in Industrial Applications

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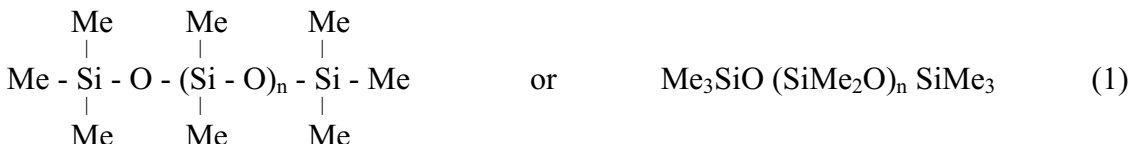
Abstract

Silicones in industry usually refer to linear polydimethylsiloxanes. A combination of properties such as their backbone flexibility, low intermolecular interactions, low surface tension and thermal stability explain many of their applications. But the name silicone also is used for more complex structures, where some of the methyl groups have been replaced by other functional groups, from branched polymers to resinous materials and even cross-linked elastomers. This allows for modifying some of the silicones properties to specific needs. The objective of this chapter is to give the curious reader a short but scientific overview of the various applications where silicones are used, including their benefits as well as limitations.

1. Introduction

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By analogy with ketones, the name “silicone” was given in 1901 by Kipping to describe new compounds of the brut formula R_2SiO . These were rapidly identified as being polymeric and actually corresponding to polydialkylsiloxanes. Among them, the most common are polydimethylsiloxanes (PDMS), trimethylsilyloxy terminated with the structure:

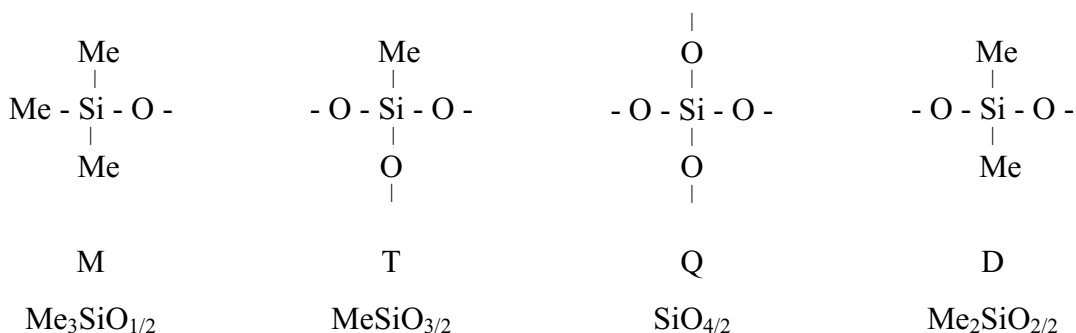


where $n = 0, 1, \dots$

The methyl groups along the chain can be substituted by many other groups (e.g., phenyl, vinyl or trifluoropropyl). The simultaneous presence of “organic” groups attached to an “inorganic” backbone gives silicones a combination of unique properties and allows their use in fields as different as aerospace (low and high temperature performance), electronics (electrical insulation), health care (excellent biocompatibility) or in the building industries (resistance to weathering).

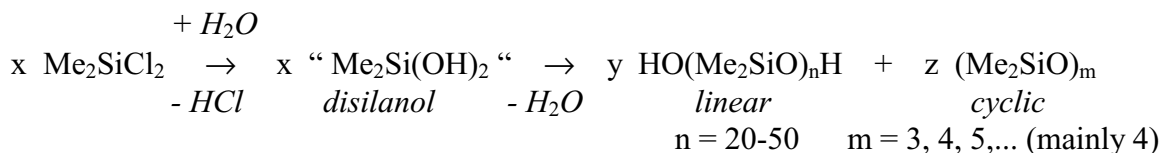
Nomenclature

The main chain unit in PDMS, $-(\text{SiMe}_2\text{O})-$, is often shortened to the letter D because, as the silicon atom is connected with two oxygen atoms, this unit is capable of expanding within the polymer in two directions. In a similar way, M, T and Q units can be defined corresponding to [1]:

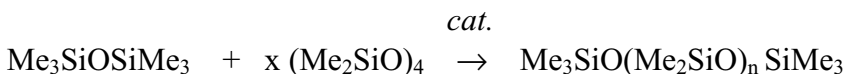


The above polymer (1) can also be described as MD_nM . This allows simplifying the description of various structures like $(\text{Me}_3\text{SiO})_4\text{Si}$ or tetrakis(trimethylsilyloxy)silane, which becomes M_4Q . Superscripts are sometimes used to indicate groups other than methyl (e.g., D^{H} for $\text{HMeSiO}_{2/2}$).

The synthesis of siloxanes has been described elsewhere [1, 2, 3]. In summary, PDMS is obtained from the hydrolysis of dimethyldichlorosilane Me_2SiCl_2 , which leads to a mixture of linear and cyclic oligomers:



Higher molecular weight PDMS is obtained after polymerisation, for example, of the above cyclics in the presence of an end-blocker such as hexamethyldisiloxane and catalysed by a strong acid or strong base according to:



Using other chlorosilanes, different end-blockers and/or different cyclics leads to many structures including polymers with various functional groups grafted on the polymer chain and/or at the polymer ends (e.g., vinyl, hydrogeno, phenyl, amino alkyl). These can be formulated into solvent-based, emulsion or solventless products.

Reactive polymers can be cross-linked into elastomers using:

- a peroxide-initiated reaction; in particular, if the silicone polymer carries some vinyl groups
- a condensation reaction; for example, between a hydroxy end-blocked PDMS and an alkoxy silane, in presence of tin salt or titanium alkoxide as catalyst
- an addition reaction; for example, between a vinyl-functional PDMS and an hydrogenomethyl dimethyl siloxane oligomer, in presence of an organic platinum complex

Such polymer, cross-linker and catalyst are formulated with various additives as one-part, ready-to-use products or two-part products to be mixed prior to use and to cure at room temperature or only at elevated temperatures.

Physicochemical Properties

The position of silicon, just under carbon in the periodic table, led to a belief in the existence of analogue compounds where silicon would replace carbon. Most of these analogue compounds do not exist, or if they do, they behave very differently. There are few similarities between Si-X bonds in silicones and C-X bonds [1-3]:

<i>Element (X)</i>	<i>Bond length (Å)</i>		<i>Ionic character (%)</i>	
	<i>Si - X</i>	<i>C - X</i>	<i>Si - X</i>	<i>C - X</i>
Si	2.34	1.88	--	12
C	1.88	1.54	12	--
H	1.47	1.07	2	4
O	1.63	1.42	50	22

Between any given element and silicon, bond lengths are longer than for carbon with this element. The lower silicon electronegativity (1.8) vs. carbon (2.5) leads to a very polarised Si-O bond, highly ionic and with a large bond energy, 452 kJ/mole (108 kcal/mol). The Si-C bond has a bond energy of ± 318 kJ/mole (76 kcal/mol), slightly lower than a C-C bond, while the Si-Si bond is weak, 193 kJ/mole (46.4 kcal/mole). These values partially explain the stability of silicones; the Si-O bond is highly resistant to homolytic scission. On the other hand, heterolytic scissions are easy, as demonstrated by the re-equilibration reactions occurring during polymerisations catalysed by acids or bases. Silicon atoms do not form stable double or triple bonds of the type sp^2 or sp with other elements, yet the proximity of the d orbitals allows $d\pi-p\pi$ retro-coordination. Because of this retro-coordination, trialkylsilanols are more acid than the corresponding alcohols. Yet, the involvement of retro-coordination is challenged [4].

Another example of the difference between analogues is the tetravalent diphenyldisilanol, $(C_6H_5)_2Si(OH)_2$, which is stable, while its carbon equivalent, a gem-diol, dehydrates. The Si-H bond is weakly polarised, but here in the direction of a hydride, and is more reactive than the C-H bond. Overall, there are few similarities between a silicone polymer and a hydrocarbon polymer.

Silicones display the unusual combination of an inorganic chain similar to silicates and often associated with high surface energy but with side methyl groups that are, on the contrary, very organic and often associated with low surface energy [4]. The Si-O bonds are strongly polarised and without protection should lead to strong intermolecular interactions. However, the methyl groups, only weakly interacting with each other, shield the main chain.

This is made easier by the high flexibility of the siloxane chain; rotation barriers are low, and the siloxane chain can adopt many conformations. Rotation energy around a CH_2-CH_2 bond in polyethylene is 13.8 kJ/mol but only 3.3 kJ/mol around a Me_2Si-O bond, corresponding to a nearly free rotation. The siloxane chain adopts a configuration that can be idealised by saying that the chain exposes a maximum number of methyl groups to the outside, while in hydrocarbon polymers, the relative backbone rigidity does not allow “selective” exposure of the most organic or hydrophobic methyl groups. Chain-to-chain interactions are low, and the distance between adjacent chains is also higher in silicones. Despite a very polar chain, silicones can be compared to paraffin, with a low critical surface tension of wetting [4]. Yet because of their low intermolecular forces, PDMS materials remain liquid in a much wider range of molecular weights and viscosities than hydrocarbons.

The surface activity of silicones is displayed in many circumstances [4]:

- Polydimethylsiloxanes have a low surface tension (20.4 mN/m) and are capable of wetting most surfaces. With the methyl groups pointing to the outside, this gives very hydrophobic films and a surface with good release properties, particularly if the film is cured after application. Silicone surface tension is also in the most promising range considered for biocompatible elastomers (20 to 30 mN/m).

- Silicones have a critical surface tension of wetting (24 mN/m), which is higher than their own surface tension. This means that silicones are capable of wetting themselves, a property that promotes good film formation and good surface covering.
- Silicone organic copolymers can be prepared with surfactant properties, with the silicone as the hydrophobic part (e.g., in silicone polyether copolymers).

The low intermolecular interactions in silicones have other consequences [4]:

- Glass transition temperatures are very low (e.g., 146 K for a polydimethylsiloxane compared to 200 K for polyisobutylene, the analogue hydrocarbon); cross-linked PDMS will be elastomeric at RT in the absence of any plasticizers.
- The presence of a high free volume compared to hydrocarbons explains the high solubility and high diffusion coefficient of gas into silicones. Silicones have a high permeability to oxygen, nitrogen and water vapour, even if in this case liquid water is not capable of wetting a silicone surface. As expected, silicone compressibility is also high.
- In silicone, the activation energy to the viscous movement is very low, and viscosity is less dependent on temperature compared to hydrocarbon polymers. Moreover, chain entanglements are involved at higher temperature and contribute to limit the viscosity reduction [4].

The presence of groups other than methyl along the chain allows modification of some of the above properties:

- A small percentage of phenyl groups along the chain perturbs sufficiently to reduce crystallisation and allows the polymer to remain flexible at very low temperatures. The phenyl groups also increase the refractive index.
- Trifluoropropyl groups along the chain change the solubility parameter of the polymer from 7.5 to 9.5 (cal/cm³)^{1/2}. These copolymers are used to prepare elastomers with little swelling in alkane or aromatic solvents.

Considering the above, many polymeric “architectures” can be prepared of different physical forms (volatile, liquid, viscoelastic, solid) with different functionalities, inert or capable of interacting or reacting with many other compounds. Formulation into convenient products leads to even more products. This explains the wide range of industries where silicones are used.

2. Characterization of Silicones

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Most analytical methods commonly used for organic materials also apply to silicones. Extensive reviews have been published about the different analytical techniques that are applicable for detecting and characterizing silicones [5]. The focus here will be on methods as they relate to typical application problems; some of these are commonly used methods. Others, such as elemental analysis and thermal analysis, are described in more detail.

Common Methods Applied to the Analysis of Silicones

Infrared spectroscopy and, in particular, Fourier transform infrared spectroscopy (FTIR), is widely available and the easiest technique for detecting the presence of silicones and obtaining information about their structure. Silicones have strong absorption bands in the mid-infrared spectrum range, at 1260, 1100-1000 and 770 cm^{-1} , meaning that levels as low as 1% can be detected. This method differentiates polydimethylsiloxane, trimethylsilyloxy groups, and copolymer-type materials. Quantification is possible using one of the strong silicone absorption peak signals. Corresponding height or area can then be correlated to a known standard and actual level calculated using Beer-Lambert's law.

Other infrared-based techniques like FTIR/ATR or FTIR/DRIFT are specifically used to detect silicones adsorbed on a substrate (see Figure 1). However, in many cases, the layer of silicone on the top of the sample surface is so thin that only the fingerprint of the bulk of the sample is seen. Better samples can be prepared through extraction using a good solvent: hexane (most alkanes are suitable), methylisobutylketone, toluene for siloxane or tetrahydrofuran for more polar copolymers like silicone polyethers. However, extraction recovery yields can be significantly lowered if the siloxane strongly bonds to the substrate. This issue is often encountered with amino-functional siloxanes.

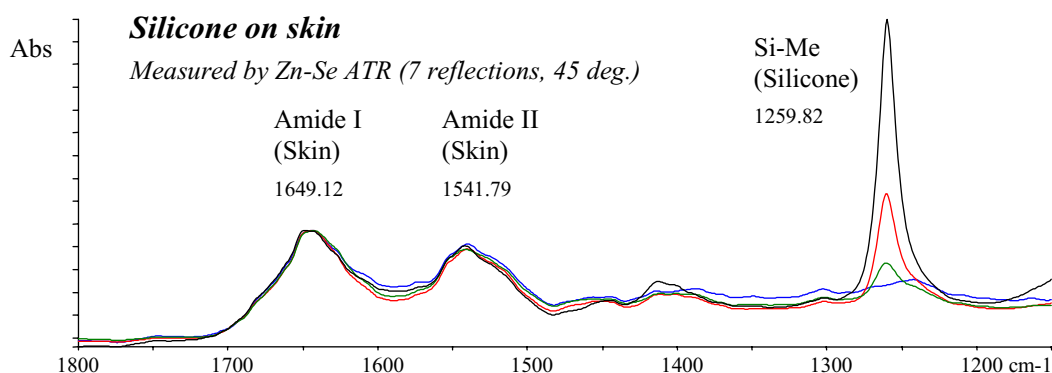


Figure 1. FTIR/ATR (attenuated total reflection) analysis of a silicone polymer applied on human skin (the amide skin peaks can be used as internal standards).

Gas chromatography coupled with mass spectroscopy detection (GC-MS) is another method used to detect silicones in a formulation, looking for the presence of siloxane cyclic oligomers, as such low molecular weight species are always associated with silicone polymers. The neat sample can be heated at a specific temperature (up to 250 $^{\circ}\text{C}$) in a headspace bottle and the generated volatiles injected. An alternative is to dissolve the sample, if feasible, and inject the solution.

The most flexible injection mode is the use of a pyrolyser coupled to the GC-MS. This allows collecting and identifying volatiles within any selected temperature range. Yet GC-MS does not allow precise quantification.

A precise quantification of those volatile cyclics is routinely done by coupling gas chromatography with flame ionization detection (GC-FID).

In addition to GC, other techniques can be used to identify and/or quantify the lowest molecular weight species present in silicone polymers; for example, gel permeation chromatography (GPC) or supercritical fluid chromatography (SFC) (see Figure 2).

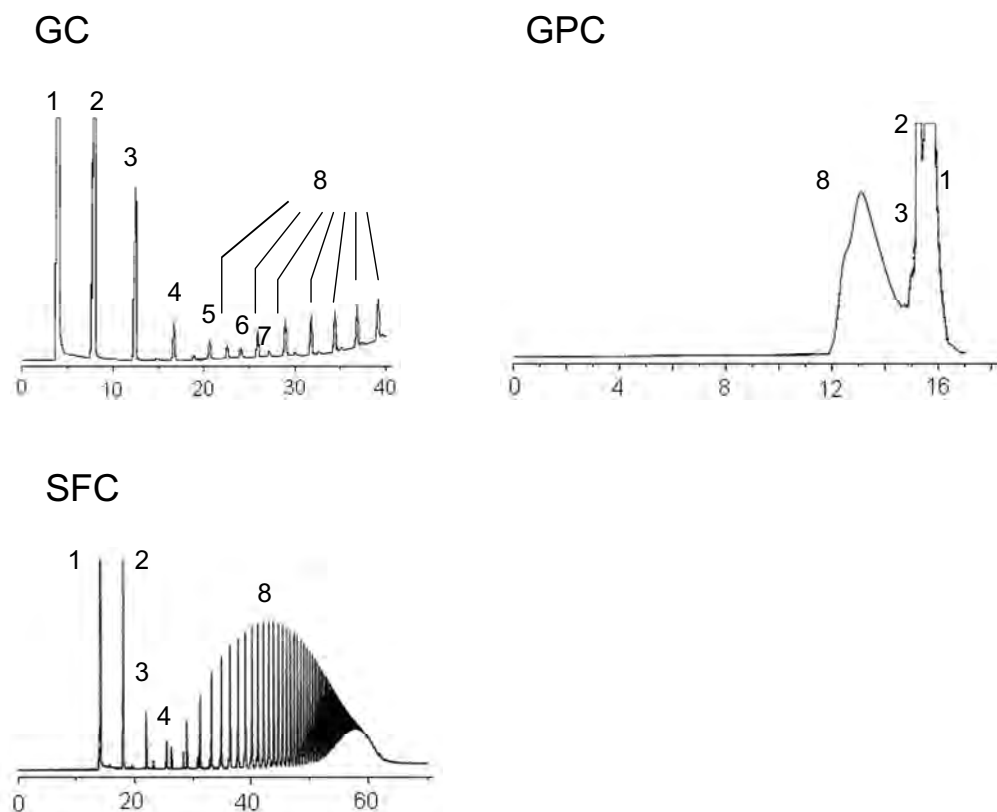


Figure 2. Comparison between different chromatographic techniques with a trimethylsilyloxy terminated polydimethylsiloxane before stripping. Peak 1 to 12 = cyclics ($m = 4$ to 10) and peak 8 = polymer.

Gel permeation chromatography (GPC) (also called size exclusion chromatography or SEC) using a refractive index detector allows one to obtain molecular weight averages and distribution information. Calibration is done with polystyrene standards, and Mark-Houwink constants are used to correlate results between the standards and siloxanes' molecular weight. Adding a laser angle scattering detector provides information on the three-dimensional structure of the polymer in solution.

In addition to infrared methods, nuclear magnetic resonance spectroscopy (NMR) can be used to obtain polymer structural details. ^1H and ^{13}C NMR bring information about the type of organic substituents on the silicone backbone such as methyl, vinyl, phenyl or polyester groups, and identify the degree of substitution in these polymers. ^1H NMR is also a technique used to measure the relative content of the SiH groups (proton chemical shift at 4.7 ppm) versus dimethylsilyloxy species (proton chemical shift close to 0 ppm). However, in some cases (e.g., as after a hydrosilylation reaction), the residual SiH levels are too low to allow for quantification. Here gas chromatography coupled with a thermal conductivity detector (GC-TCD) is a more appropriate method. This method works in an

indirect way, analyzing the hydrogen generated when the sample is hydrolyzed in presence of a strong base as a catalyst.

Application Specific Methods for the Analysis of Silicones

In addition to the methods described above, some more specific techniques are used to detect the presence of silicones as formulation ingredients or contaminants or to study their high/low temperature behaviour.

Atomic absorption spectroscopy (AAS) allows quantification of the silicone element in a given formulation. This approach is widely used to quantify the silicone content in materials made of, treated with or contaminated by silicones.

If the formulation is known not to contain any other silicone element source than silicones, the presence of silicones can be easily detected by X-ray fluorescence (XRF), as the method does not require any particular sample preparation. XRF is capable of measuring silicone contents if standards can be prepared in the same matrix as the formulation.

Surface tension measurement is another easy way to detect surface contamination by siloxanes, through comparison with a virgin reference. Contact angles of both suspected and clean surfaces are measured with a set of suitable liquids. Silicone contamination will be indicated by large contact angles resulting from a significant decrease in surface energy.

X-ray photoelectron spectroscopy (XPS) or time of flight-secondary ion mass spectrometry (TOF-SIMS) are more sophisticated techniques that can also be applied to detect and characterize silicones within the 10-50 Å depth layers from the surface of materials.

The average structure of silicone polymers is accessible through ^{29}Si NMR thanks to the ^{29}Si isotope nuclear spin ($I = \frac{1}{2}$) and its relative abundance (4.7%). However, the relative sensitivity of ^{29}Si NMR is low versus ^1H NMR ($7.8 \cdot 10^{-3}$ times lower), which implies long accumulation times for any measurements. Peak assignments are eased by large chemical shift differences and the use of decoupling (see Table 1). Yet silicone chain ends can not always easily be detected by ^{29}Si NMR, especially in high molecular weight siloxane polymers.

For structural purposes, a complementary technique to ^{29}Si NMR has been developed by depolymerizing the siloxane backbone in the presence of an excess of an appropriate end-blocker using a strong base or acid as catalyst. The recovered volatile oligomers are then quantified by GC-FID. This approach has proven applicable to quantifying traces of silicones on substrates like wool, paper or hair [6].

Table 1: Typical ^{29}Si NMR Chemical Shifts

<i>Unit Structure</i>	<i>Unit Type</i>	<i>Chemical Shift</i>
$\text{Me}_3\text{SiO}_{1/2}$	M	+ 7 ppm
$\text{Me}_2\text{SiO}_{2/2}$	D	- 22 ppm
$\text{MeSiO}_{3/2}$	T	- 66 ppm
$\text{SiO}_{4/2}$	Q	- 110 ppm
$\text{HOMe}_2\text{SiO}_{1/2}$	M^{OH}	- 10 ppm

The performance of silicones versus organic polymers at high or low temperatures is verified when using thermal analysis methods such as thermogravimetric analysis (TGA) or differential scanning calorimetry (DSC), whether under air or inert atmosphere. In the latter conditions, the onset of polymer depolymerisation to cyclic species is usually found at temperatures higher than 350 °C. However, traces of base or acid are sufficient to significantly decrease the temperature at which decomposition starts to occur by catalyzing the re-equilibration of the polymer into low molecular weight volatile species. TGA is the most appropriate technique for measuring the onset of weight loss (temperature ramp mode) or the amount of weight loss at a fixed temperature (isotherm mode).

It is recommended to run TGA under inert atmosphere as the presence of oxygen will allow, at temperature higher than 300 °C, the partial oxidation of the silicone chain groups into silica and the formation through methyl substituents oxidation into species like carbon monoxide, carbon dioxide, formaldehyde, hydrogen and water. However, unlike GC-MS techniques, TGA does not give information about the nature of the species volatilized (see Figure 3).

On the other hand, DSC is particularly appropriate for analyzing the behavior of silicones at low temperatures. Due to the flexibility of the polysiloxane backbone, glass transition typically occurs below -120 °C, a remarkably low temperature if compared to other polymers. This is why polydimethylsiloxanes remain fluid and silicone elastomers remain flexible at low temperatures. Nevertheless, crystallization can be made to occur, at least for a fraction of the polymer, on slow cooling below -40 °C. The cooling rate should be low enough to allow chains to form crystalline structures. Silicone polymers can also be supercooled to a glassy state without crystallization under fast cooling or quench. In this case, on reheating, a cold crystallization exotherm is observed followed by the usual endotherm(s) around -50 °C (several “melting points” can be observed as multiple crystallization/melting events occur in the sample in the same temperature range) (see Figure 4).

TGA ST-Elastomer 10

Comment: under nitrogen

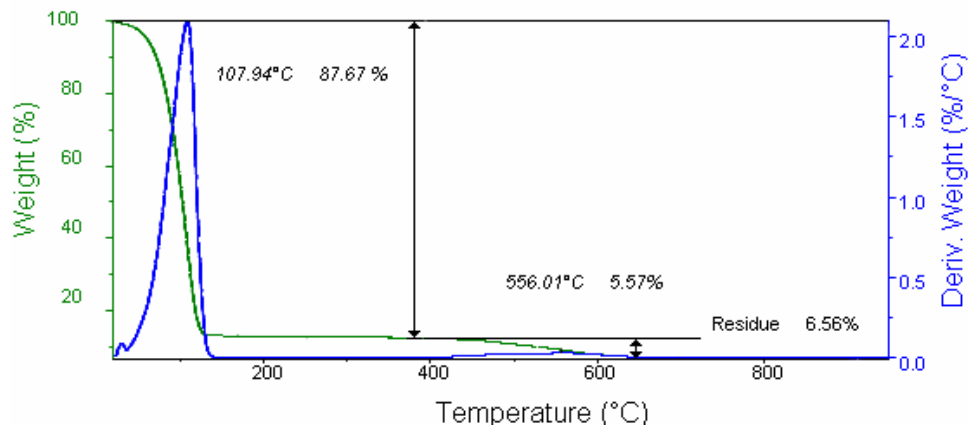


Figure 3. TGA analysis under dry nitrogen of a blend of silicone volatile species and silicone elastomer (weight loss curve in green, first derivative curve in blue); precise content in volatile species (weight loss up to 150 °C) and in elastomer (second weight loss step between 400-700 °C and residue in 950 °C).

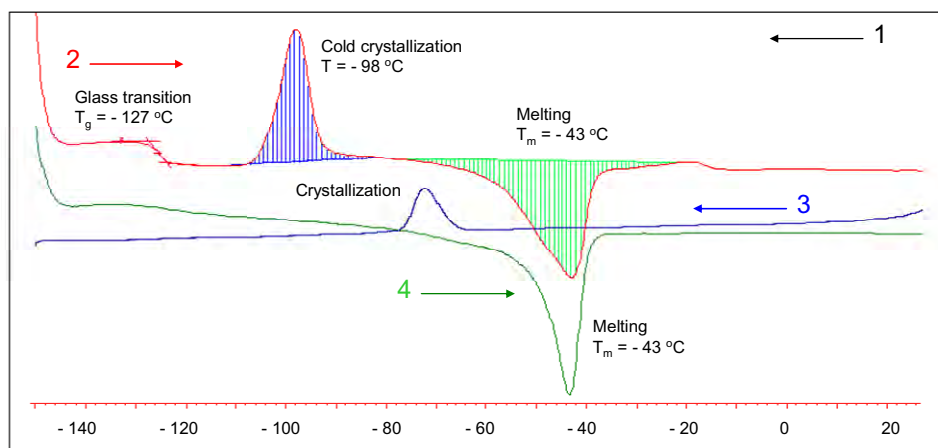


Figure 4. Typical low temperature DSC analysis of a silicone elastomer: the sample is super-cooled at -150 °C (1 - black / no curve), then heated from -150 °C to 25 °C (2 - red curve). The following are detected: glass transition (T_g) at -127 °C, cold crystallization at -98 °C and melting (T_m) at -43 °C. Afterwards, the sample is cooled down at a low cooling rate and reheated. A crystallization exothermic peak is observed during the cooling step (3- blue curve) and only a single melting endothermic peak during the second heating step (4 - green curve).

DSC is also a powerful technique for studying exothermic reactions such as the hydrosilylation reaction, which is associated with a strong exotherm. Dynamic or isotherm modes allow characterization of the cross-linking and optimization of formulations based on the temperature corresponding to the onset of cure or to the maximum cure rate (see Figure 5).

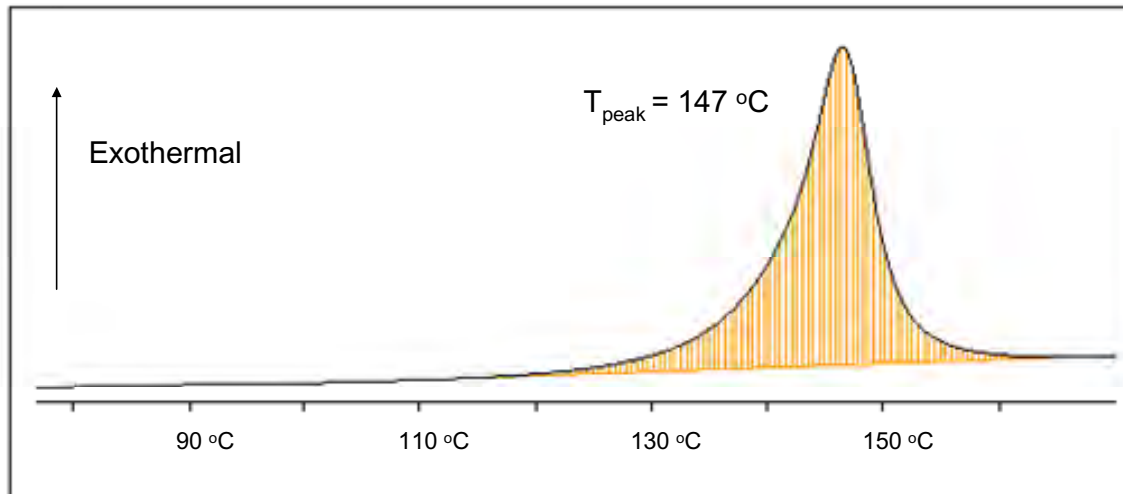


Figure 5. *Differential scanning calorimetry of the reaction between silicone polymers with SiVi groups and polymers with SiH groups in presence of a platinum catalyst.*

3. Silicone in the Food Industries

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In food-related processes, silicones are very much associated with foam control agents because of the low surface tension displayed by polydimethylsiloxanes, and because this is a key property for formulating an effective antifoam. Foam control is critical here as in many other industries, as excessive foaming slows processes and can reduce volume efficiency.

Polydimethylsiloxanes as Surface-Active Ingredients in Antifoams

Silicone oils, or in particular polydimethylsiloxane (PDMS) materials, combine many unusual properties because of their molecular characteristics, such as the flexibility of the Si-O-Si backbone and the very low cohesive energy existing between methyl groups. PDMS polymers have low surface tension, and most of them are nonvolatile and remain liquid even at quite high molecular weights. They are also highly insoluble in water.

Because of the extreme flexibility of the siloxane backbone and ease with which various polymer configurations can be adopted, and despite the siloxane backbone's considerable polarity, it is the polymer side groups that are the primary surface-active entities in the polymer structure (see Section 1).

The pendant groups in PDMS are methyl groups, which show the weakest intermolecular interactions known: the London dispersion forces. The low surface tension, which is a direct manifestation of low intermolecular forces, confirms that the interactions between two PDMS chains occur only through their methyl groups. The polymer backbone

controls the organization of the side groups at the surface, and its flexibility has a major effect on the ease with which the pendant groups can adopt preferred configurations. Thus, from a surface tension standpoint, the more flexible the backbone, the more readily will the lowest surface energy configurations be adopted. PDMS is a particularly favored case of very low intermolecular force pendant groups anchored along the most flexible backbone, thus allowing the methyl groups to be ideally presented to the external world.

It is often observed that neat silicone oil shows low efficiency as antifoaming agent. But mixtures of such oils with hydrophobic particles such as treated silica or finely divided high melting point waxes are generally much more effective than the individual components [7-8-9-10]. In fact, the mixture performs well even if each component is ineffective when used alone. This synergy is observed for most combinations of oils and solids and in various types of foaming media. Effective foam control agents continue to be developed using such combinations to adjust for different types of foam problems.

Many foam control agents are added to the foaming medium after being predispersed in water, either as self-dispersible neat materials, oil-in-water emulsions, or self-dispersible mixtures or compounds. This is because it is critical to have small droplets of antifoam in the liquid medium to have antifoaming activity. To rupture a foam film, an oil/hydrophobic particle droplet must in a first step emerge from the aqueous phase into the air-water interface during a process called entering. After this entering, some oil from the droplet can spread on the solution-air interface in a second step.

Two coefficients measure the changes in the free energy of the system associated with these two steps.

When an oil drop enters the air-water interface, the change is measured by the entering coefficient, E :

$$E = \sigma_{AW} + \sigma_{OW} - \sigma_{OA}$$

A positive E means the surface tension of the antifoam liquid (σ_{OA}) is lower than the sum of the surface tension of the foaming liquid (σ_{AW}) and the interfacial tension between the antifoam and the foaming liquid (σ_{OW}). This value is the opposite of the free energy associated with the entering step.

When an oil drop spreads over the air-water surface, change is measured by a spreading coefficient, S :

$$S = \sigma_{AW} - \sigma_{OW} - \sigma_{OA}$$

In this step, the water surface is replaced by an oil surface. A positive S means the surface tension of the foaming liquid (σ_{AW}) is greater than the sum of the surface tension of the antifoam liquid (σ_{OA}) and the interfacial tension between the antifoam and the foaming liquid (σ_{OW}). The free energy associated with this change is the difference between the

energy of the end result (the sum of the oil-water interfacial tension and the oil surface tension) and the starting point (the water surface tension). The spreading coefficient is the opposite of the free energy change associated with the spreading step.

Both the entering coefficient and the spreading coefficient must be positive for the corresponding processes to be energetically favorable.

Entering is obviously essential to foam rupture, and it is generally agreed that the entering coefficient must be positive for a particle or droplet to cause rupture of a foam film.

A recent study suggests that spreading of a layer of oil eases the foam breaking mechanism, suggesting that the ability to spread is an important property for an oil used in antifoam formulations [11].

For both the entering and spreading coefficient to be positive, it is important to have a liquid with a low surface tension, which is the case with silicone oils.

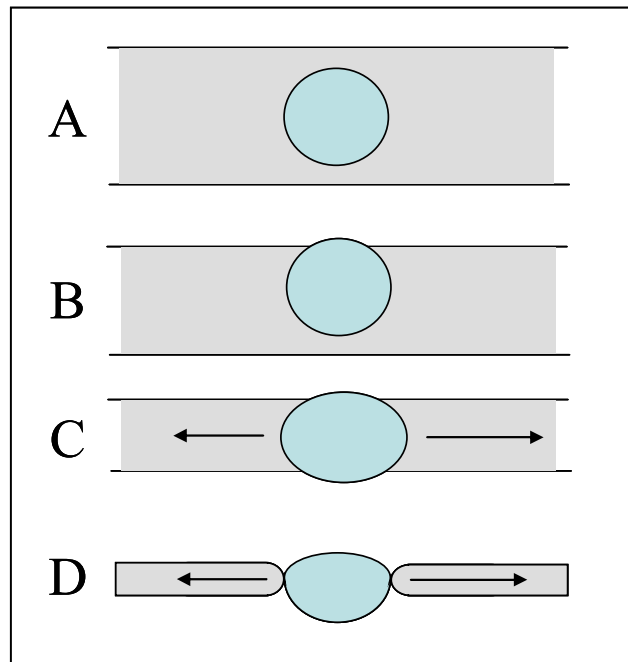


Figure 6. *Schematic presentation of the bridging of a foam film by a spherical antifoam droplet. In A, the antifoam droplet is entirely in the liquid film. In B, the antifoam droplet has entered the surface. In C, the antifoam droplet bridges the film. In D, the process of bridge dewetting occurs, leading to destabilization of the foam film and eventually to foam rupture.*

It has been shown that hydrophobic particles ease entry of the antifoam droplet in the foam walls or film interfaces, explaining the benefit of their addition in antifoam formulation [8].

Once the silicone antifoam droplet has entered the two air-water interfaces (Figure 6), it forms an oil bridge between the two surfaces of the foam film. One of the mechanisms

proposed in the literature involves at this stage the dewetting of the solution away from the antifoam droplets, because of the low surface tension of the oil, and leading eventually to the film rupture.

Although this is a simplified view of the mechanism of antifoam action, it helps explain why silicones are very effective for rupturing foam.

Food and Beverage

Foods are chemical mixtures consumed by humans for nourishment or pleasure. Most of the nutrients are provided by proteins, vitamins and minerals, whereas carbohydrates and fats provide energy. But any media containing such biomaterials and proteins with or without carbohydrates show high foaming tendencies. The proteins act as surfactants due to their amphiphilic structure. They can unfold and strongly adsorb at the interface, forming strong intermolecular interactions. This produces a viscoelastic, irreversibly adsorbed layer at the air-liquid surface, which stabilises the foam. These kinds of films are not easily broken.

This explains why foam is often encountered during food handling, from production to end use. But uncontrolled foaming media are a source of severe loss of production capacity, including inefficient mixing or pumping, downtime from clogged lines, overflows, spillage hazards and product waste. Therefore, foam control technologies (either mechanical or based on chemical additives) have been developed to overcome these problems and reduce costs to a minimum [12-13-14].

Chemical additives designed to reduce such foaming problems are called antifoam agents, foam control agents or defoamers. But the choice of ingredients for applications in the food industries is limited because of regulations and the need to ensure that such ingredients do not cause harmful effects.

Silicone oils are effective ingredients in antifoaming agents. In food and beverage applications, only PDMS materials are used because of their low surface tension, water insolubility, thermal stability and chemical inertness. PDMS of sufficient molecular weight does not penetrate through biological membranes, and orally is not metabolised, but excreted unchanged (see Section 21). These PDMS materials are mixed with hydrophobic particles and formulated as powders, compounds or emulsions.

The pathway followed by food materials starts from their production (e.g., plant growth), their processing and their uses. Foam can be produced in each of these steps.

Silicone Antifoams in Food Production. Crop treatment often requires the spraying of various chemicals on plant leaves. Surface active materials, including silicones such as silicone polyethers, are often needed to help the wetting of the very hydrophobic plant leaves. This is often associated with foaming problems and antifoams are required; for example, during tank-filling operations.

Silicone Antifoams in Food Processing. In the production of sugar from sugar beets, foaming is a serious problem, starting from the beet-washing stage to diffusion and evaporation stages. The foam is attributed to the numerous nonsugar materials present, such as cellulose, lignin, protein, vegetable bases (betaine and choline), and especially saponin [15]. Foam controllers employed in the beet-washing process are likely to appear in wastewaters. Therefore, their environmental profile is important to consider. Because sugar is intended for human consumption and trace amounts of antifoaming agents may be present in the finished product, various legal and health issues must also be considered. Furthermore, steam-volatile components must be avoided during the evaporation and boiling steps.

Fermentation processes such as the production of drugs, yeasts or simply ethanol require antifoams to control the level of foam during the microorganisms' growth and the end-product formation. Biomaterials in the growing media often have a high foaming tendency, whether they are present in the blend of several carefully selected materials like protein extract, sugar, or as byproducts of other food production processes like sugar cane, sugar beet molasses or corn liquor production. On top of this, proteins are often produced by microorganisms and released during the fermentation process, making the foam harder to control. Apart from their essential antifoam properties, the ideal foam control agent for fermentation processes should not be metabolized by the microorganisms, be nontoxic to these microorganisms and to humans, should not cause problems in the extraction and purification of the final product, should not have detrimental effects on oxygen transfer and be heat sterilizable.

Processing potatoes or vegetables requires a wash bath. Intensive foaming of potato juice, starch slurry and processing water is caused by proteins, other nitrogenous compounds and starch found in potatoes or vegetables. Starch foam is very stable and difficult to counter, and antifoam is the most practical and universal application solution.

Beverages are also prone to foam problems during filling and bottling of alcohol beverages, coffee drinks, flavored water and fruit drinks, or when reconstituting powdered drinks like instant coffee or tea with water.

Typical foam control agents recommended for use in food processing or packaging must:

- have Kosher certification
- comply with FDA Regulation 21 CFR 173.340 (secondary direct additives).

Silicone Lubricating Oil in Food Processing

Silicones suitable as food grade lubricating oils are generally straight-chain PDMS. They may be formulated with treated fume silica to obtain a grease and the right rheology profile, including a yield point (see Section 18).

Silicone lubricating oil with incidental food contact must meet FDA regulation 21 CFR 178.3570.

Immiscibility with many organic fluids, low temperature dependence of their physical characteristics, physiological inertness and high temperature stability are some of the key

properties making silicone lubricating oils better than organic alternatives for these applications.

Silicone lubricating oils are used in bearings, gears with rolling friction, on plastic surfaces and on rubber parts encountered on equipment used for food processing (see Section 18).

4. Silicones in the Pulp and Paper Industry

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Organosiloxane materials can be found throughout the processing of pulp and paper, from the digestion of wood chips to the finishing and recycling of papers. Some examples are:

- As digester additives, silicones improve the impregnation of active alkali in the wood chips and improve the cooking
- As antifoams, silicones help de-airing or drainage in the pulp washing and paper-making processes
- As additives, silicones contribute in the finishing process of paper and tissues
- In the recycling of papers, silicones act as de-inking aids

Some specific examples are developed here to demonstrate how the properties of silicones can bring benefits as antifoams in the paper pulp-washing process and as softening agents in the treatment of tissue fibers.

Antifoam in the Pulp-Washing Process or Brownstock Washing

Kraft or sulfate pulping remains the most common chemical process used to produce bleached and unbleached pulp of high quality [16]. The wood chips are impregnated with an alkaline liquor containing NaOH and Na₂S and digested at high temperatures. During this process, delignification and degradation of esters from fatty acids, resin acids and sterols occurs. This generates surface-active molecules that create excessive foam during the pulp-washing process. The presence of foam is a serious problem for the paper mill operator since it dramatically reduces washing efficiency, and in extreme conditions, can lead to an overflow from the filtrate vat spilling onto the washroom floor. In some cases, such an event can cause the shutdown of production.

Both organic and silicone antifoams are used and subjected to harsh conditions of pH (11 to 12.5) and temperature (80 to 95 °C). Antifoams are typically based on a combination of a hydrophobic and insoluble oil formulated with hydrophobic solid particles (see Section 3). These mixtures are generally called antifoam compounds [17]. Organic antifoam compounds are generally based on mineral, paraffin or vegetable oils and particles made of amide waxes like ethylene-bis-stearamide (EBS) or hydrophobized silica. Silicone antifoams are usually made of polydimethylsiloxane (PDMS) fluids compounded with hydrophobized silica.

Silicone antifoam compounds are sometimes combined with more hydrophilic organic polyethers or silicone polyethers, which can help the emulsification of the silicone compound and act as co-antifoam agents if their cloud point is below the application temperatures.

To control foaming over a long enough period of time, organic antifoam must generally be added at higher dosage levels (0.5 to 5 kg/t, expressed as kg of antifoam per ton of dried pulp) if compared to silicone-based antifoams (0.2 to 0.8 kg/t).

In the most modern paper mills designed to run at high production rates but also with minimum water consumption, the washing of fiber stocks containing high soap levels as from Scandinavian softwoods or from birch is done under such harsh conditions that only silicone antifoams give the required level of performance. Silicone antifoams contribute to various effects in the process: as defoamers, they reduce the amount of foam immediately after their addition (this is called the “knock down” effect), but as antifoams they also prevent further foam formation and maintain their activity over a long period of time (this is called “persistency”). Silicone antifoams also help drainage and improve washing efficiency by reducing the level of entrapped air in the pulp mat [18].

Silicone antifoams for pulp and paper applications can be seen as a combination of polydimethylsiloxane (PDMS) chemistry, silica chemistry (as silica surface treatment is critical), and emulsion technology, as emulsions are sometimes the preferred route of delivery for the antifoam. Since its introduction in the pulp market in the early 90s, the technology of silicones as antifoams and drainage aids has dramatically evolved. Key improvements worth noticing in recent years are two-fold:

- Improvement in persistency, which allowed a dramatic reduction in dosage level
- Optimization of the way the antifoam active is delivered and dispersed in the processing media

Both are critical for reducing the risks of undesired antifoam hydrophobic deposits from these foam-control agents. Lower dosage reduces the amount of hydrophobic particle present, and improved delivery from specific emulsions (particle size, stability) reduces the risk of agglomeration of such insoluble components.

The persistency of silicone-based antifoams has been improved using PDMS polymers of very high molecular weight that are more resistant towards deactivation [19], less prone to emulsification upon use and have less tendency to liberate the hydrophobic silica particle if submitted to high shear. Careful selection of the silica used (structure, surface area, particle size, porosity) is key to achieving optimum performance of the silicone-based antifoam.

Silicone-based antifoams are used at very low levels and generally formulated as self-dispersible concentrates or even more commonly as water-based emulsions. This allows a dramatic reduction in problems of pitch deposits that are commonly encountered with nonaqueous mineral oil/EBS-based antifoams [20].

Finally, over and above any technical requirements, antifoams for paper and pulp applications must meet acceptance under FDA Indirect Food Contact Guidelines 21 CFR 176.170, 180 or 210 and compliance with BGA Recommendations XV.1.A. and XXXVI.B.C1. These regulatory requirements are fulfilled by many silicone-based materials.

Silicone Finishes in Tissue Converting

Silicone materials are used as a surface treatment for tissue softening to enhance the performance of bath, toilet and facial tissues; paper towels, napkins and tablecloths; wet and dry wipes; and other consumer and commercial paper products [21].

Similar to other applications such as textile finishing, fabric treatment or hair care, a wide range of performance results from the use of silicones. Most new products for tissue converting are water-based, solventless emulsions. Silicones provide softening by reducing the coefficient of friction without reducing wet or dry strengths, providing antistatic properties and reducing dust and lint during use. More hydrophilic silicone polyethers can also enhance water and liquid absorbency.

5. Silicones in the Textile Industries

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In the textile industries, silicones are used in all stages of the process, on the fiber during production, on the fabric and/or directly on the finished goods. Silicones are applied from different delivery systems to provide various benefits like lubrication, softening, foam control or hydrophobic coatings.

Silicones in Fiber Production

Higher production rates oblige artificial fiber producers to continuously search for more efficient materials to lubricate fiber and spinneret and to avoid excessive overheating due to friction during high-speed manufacturing [22-23].

Because of properties such as heat stability and good lubrication, silicones can provide a reduction of the dynamic coefficient of friction, reducing the risk of fiber melting and breakage during production (see Section 18). Low viscosity polydimethylsiloxane (PDMS) is generally used in combination with solid particles (e.g., those made of magnesium stearate), as this also reduces the static coefficient of friction.

During the manufacturing of artificial fibers, PDMS can also be used as a lubricant to avoid adhesion of the thermoplastic fiber material to the spinneret, which would cause unstable production and cleaning issues.

Silicones can also be used to achieve low coefficients of friction between the fibers themselves. Generally a silanol-functional silicone, a reactive cross-linker (e.g., a silane or an

epoxy-functional silicone) and a condensation catalyst are formulated together into a coating to encapsulate the fiber. Such treated fibers will lead to high thermal insulating textiles and filling material for fiberfill systems as found in duvets or overalls.

Cleaning silicones used during fiber production can sometimes be an issue. To minimize this, lubricant silicone polyethers have been developed with higher hydrophilicity and easier to clean (see Section 7).

Silicone as Fabric Softeners

Once produced, fibers can be treated with silicones to impart initial softness to the textiles made from these fibers. Softening is considered to come from the siloxane backbone flexibility and the freedom of rotation along the Si-O bonds. This allows exposure of the low interacting methyl groups, reducing fiber-to-fiber interactions.

To enhance durability through multiple wash cycles, some methyl groups can be replaced on the silicone polymer by other functional groups to increase the silicone softener attraction to, and interaction with, the fibers to be treated.

In this respect, amino-functional groups like $-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{NH}-\text{CH}_2-\text{CH}_2-\text{NH}_2$ are particularly popular for increasing physical adsorption and providing better softening properties.

During the application generally done in acidic conditions, these amino groups are quaternized to cationic species ($-\text{NH}_3^+$), which have a stronger attraction for the negatively charged fabric. This is particularly true for cotton-based fabrics, which carry anionic charges on their surface. This improves deposition, performance and durability of the softener coating.

These amino-functional silicones are best delivered to the textile surface under the form of a microemulsion. This offers a number of advantages if compared to macroemulsions. The quality of a microemulsion is easily controlled: visual appearance and good clarity ensures small particle size and long shelf life without the need of any sophisticated particle size testing equipment. Microemulsions have also excellent shelf stability and allow for higher dilutions with better shear stability.

On the other side, microemulsions are often formulated with high levels of surfactants, and these can affect the softness normally provided by the silicones. Such surfactants must therefore be carefully selected.

Amino-functional silicones can also yellow upon aging via chromophores generated on the amino group, in particular from linkages between amino groups. Modifying the amino groups with adequate blocking groups overcomes this problem, offering formulators non-yellowing fiber softeners [24].

Silicones will inherently increase the hydrophobic nature of any treated fabric, a feature not desired in some applications; for example, as it results in poor water absorbency on towels. Trends here are to design amino-functional silicone polymers with higher hydrophilicity [25].

Silicones as Process Aids

As in many other processing industries, silicones are widely used in the textile industries as antifoams (see Section 3). Silicone antifoams can operate in a wide range of temperature and pH conditions and can manage highly foaming media. Their compositions can be complex, but there are some formulation rules well known to the silicone industry for producing highly efficient antifoams for many different applications and in various foaming media. Conditions are so diverse that a “universal” antifoam has not yet been formulated.

In the textile industry, the main use of antifoams is during the scouring step, which is the cleaning of raw fibers before further processing or during the finishing step. Both of these are high foaming steps, as surfactants are extensively used to clean, or in the formulation of fabric softener emulsions. As the industry is also trying to minimize the amounts of water used in such process steps, this results in even higher surfactant concentrations.

The greater use of high-shear jet machines requires antifoam emulsions that are stable under very high shear to avoid undesired localized deposition of silicone polymers. Such deposition can result in staining problems.

Other process aids include:

- Needle lubricants or PDMS fluids to avoid needle overheating during sewing
- Silicone polyethers to facilitate the wetting of difficult substrates that contain high levels of organic fats in their structures

Silicones as Hydrophobic Agents

Silicones provide very hydrophobic finishes on various fabrics. This treatment involves full fabric impregnation from silicone-in-water emulsions, usually via a padding process.

The silicone phase of such emulsions contains SiH-functional polymers because of their reactivity towards the fabric, but also because these polymers can cross-link with each other into a hydrophobic and durable fabric treatment, particularly if formulated with a suitable catalyst [26].

Silicones in Fabric Coatings

Silicones are not limited to fiber processing or finishing. Their use extends as coatings in diverse applications, from fashion wear such as women’s stockings to technically demanding air bags (see Section 14). Applications here call for substantially thicker coatings, with typical coating weights up to 10 to 800 g/m².

These applications are based on cross-linked silicone polymers or elastomers, which can be formulated into crystal-clear coatings that can be either soft and flexible or hard and rigid. All such coatings have very similar compositions and share common raw materials for up to 70% of their formulation. They perform well over a wide range of temperatures and with better thermal stability characteristics than organics.

Apart from one-part RTV (Room Temperature Vulcanisable) elastomer used in women's stockings, liquid silicone rubbers (LSRs) are today the preferred material for such fabric coatings because of their ease of use and rapid cure when exposed to elevated temperatures. Cross-linking in these elastomers is achieved by the addition of SiH functional polymers to SiVi functional polymers using a platinum catalyst (see Section 9).

These LSRs, as other silicone elastomers, contain fume silica, as such fillers dramatically improve mechanical properties (see Section 14). However, compared to other silicone elastomers with high mechanical properties such as high consistency rubbers, LSRs can be metered/mixed with pumps and easily dispensed as coatings on various fabrics [27].

Silicone coatings remain flexible even at very low temperatures, typically -100 °C. Service life has been reported as 30,000 h at 150 °C and 10,000 h at 200 °C in air. When needed, additives such as cerium or iron oxides can be used to further improve heat stability [28].

Compared to many organic elastomers, silicones do not contain organic plasticizers. They are therefore not prone to plasticizer migration problems or embrittlement due to plasticizer evaporation or degradation.

Other properties make LSRs desirable as coating materials (see Table 2):

- Solventless compositions with long bath life at room temperature and low viscosity, (15,000 mPa.s) and therefore easy to process in coating operations using methods like “knife over roller” or “knife over air”
- Fast cure at elevated temperatures (e.g., 1 to 2 minutes at 160 °C)
- Good adhesion to various coated substrates like glass, polyamide or polyester fabrics
- Good visual appearance
- Adequate data to satisfy relevant regulatory requirements (e.g., food grade, skin contact).

Table 2. Typical Properties of LSRs Used in Fabric-Coating Applications

Mixed viscosity, <i>mPa.s</i>	15,000 - 200,000
Tensile strength, <i>MPa (psi)</i>	3.5 - 9.0 (500 - 1300)
Elongation at break, %	100 - 800
Tear strength, <i>kN/m (ppi)</i>	5 - 40 (28 - 230)
Hardness, <i>Durometer Shore A</i>	15 - 70

In many cases, the prime purpose of silicones in such fabric coatings is to provide some form of protection from exposure to high temperatures (as in conveyor belts), low temperatures (as with many outdoor goods) or exposure to stress over long periods of time (as in air bags or compensator bellows) (see Table 3). In such applications, silicones are more stable than other elastomers.

Table 3. Typical Applications and Key Properties of Silicone Elastomer Fabric Coatings

<i>Coating type</i>	<i>Application area</i>	<i>Key properties</i>
Soft coating	Hold-up stockings (RTV)	Ease to process Crystal clear Soft Non slip/high elongation
	Outdoor clothing and tents (LSR, RTV)	Adhesion Flexible Thermal stability Colorless Hydrophobicity
	Air bags (LSR)	Strength Adhesion Slip Stability at elevated temp.
Hard coating	Conveyor belt coating (LSR)	Adhesion Non slip/abrasion resistance Thermal stability Food grade
	Compensator bellow (LSR)	Adhesion Chemical/Thermal stability abrasion resistance
	Medical protective wear (LSR, RTV)	Hydrophobic Autoclavable Adhesion

6. Silicones in Household Cleaning Applications

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Silicones and household cleaning applications have been associated for more than 50 years, particularly in the laundry area, where the main use is foam control in consumer washing machines and fabric softening. But silicones are also used to provide extra benefits such as fabric dewatering, antiwrinkle characteristics, ease of ironing or improved water absorbency. Silicone additives have also been developed to reduce fabric mechanical losses over time or to improve perfume release.

Silicones as Foam Control Agents

A wide range of foam control agents exists. These foam control agents prevent (antifoams), and knock down (defoamers) foam that occurs in both the manufacture of detergents and during their use by consumers at home, or by professionals.

Antifoams are critical in many consumer applications. For example, in a washing machine, a steady control of foam is needed, rather than its complete elimination or prevention. Correct foam control is essential since consumers are very perceptive about foam levels. Moreover, incorrect foam levels can reduce the detergent's cleaning efficiency.

Silicone foam control agents are based on combinations of polydimethylsiloxane (PDMS) and finely divided silica particles. This particular combination seems most effective (see Section 3).

To optimize antifoam performance, the foam control agent must be properly incorporated into the detergent product with an effective protection system so it will subsequently disperse into the wash liquor in the right form. Silicone antifoams have been developed either as compounds, ready-to-use emulsions for liquid detergents or solid powdered forms that are easy to incorporate in powder detergent formulations. Delivery form and stability of the silicone antifoams (i.e., protection from the detergent under various temperature or humidity conditions) are critical aspects.

Silicone antifoams are also used in the manufacture of detergents to help processing of detergent liquids, to de-air the wet slurry and improve powder density in the spray-drying towers for powdered detergents, or to facilitate all types of bottle-filling operations.

Silicones for Delivering Fabric Care Benefits

Within the textile industry, silicone products have been used for almost 50 years. The primary textile benefits and applications from silicones have been as antistatic agents, fibre and thread lubricants during fabric production, and antifoaming and fabric softening agents during the fabric-finishing step (see Section 5).

It is known from both the textile and laundry industries that the laundry wash cycle process removes most of these fabric finishes. It is considered that about 10 wash cycles are sufficient to remove most of the garment's initial fabric treatment.

With ever-demanding consumers having less time for clothing care, wanting clothing to look better and as new as possible after repeated washings, and expecting clothes to be comfortable directly from the dryer, it became a market need to deliver the known textile industry technology benefits in consumer laundry products.

Key technologies and silicone product parameters in fabric care are:

- Polymer architecture and functionality

- Type of delivery vehicle
- Particle size properties of emulsion vehicles
- Surfactant systems used with emulsion vehicles

The association of a flexible backbone with low intermolecular interactions as limited to methyl groups explains the lubrication characteristics of PDMS (see Section 5). Some methyl groups can be substituted by other groups, such as hydroxy, amino, amido, polyether and longer alkyl, either along the chain (grafted) or at the ends of the chain (end-blocked). These functionalities allow adjustment of the architecture of the polymer to tailor the interactions between these polymers and the fabric during and after laundry. Some polymers can be cyclic, but the majority are linear with various molecular weights, from volatile fluids to high consistency gums. They can also be cross-linked to variable levels to provide higher substantivity, controlled spreading and elastomeric properties.

Depending on the requirements of the application, the above silicone polymers can be delivered as self-emulsified in the formulation (polyethers), emulsified in situ (low molecular weight amino-functional polymers) or pre-emulsified (most polymers). Some formulations may contain volatile silicones as a secondary delivery system within the emulsion.

Silicone emulsions are available either as microemulsions (<100 nm) or macroemulsions (>100 nm), depending on the polymer architecture and functionality selected. The emulsion particle size is often related to the properties ultimately observed on a fabric. Microemulsions are able to penetrate into the yarns and deposit onto the fabric fibers, bringing a soft, dry feel to fabric. Studies suggest that the deposition of silicone is internal, which provides dry lubrication of individual fibers against each other with a very thin coating of silicone, probably reducing the static coefficient of friction. Macroemulsions deposit on the external surface of the fabric, causing superior lubrication through reduction of the dynamic coefficient of friction. They provide relatively good fabric softening performance.

Silicone emulsions may be formulated with adequate anionic, nonionic or cationic surfactants. The choice is driven by the compatibility with the application formula and the mechanism of silicone action or deposition. To provide its benefits, the silicone must generally deposit on the fabric. This deposition is triggered either by the polymer functionality and/or by the emulsion surfactant system used in synergy with the application formulation.

Fabric Softening. Numerous patents have been filed [29-30] on this application since 1976, and many commercial product implementations exist [31], mainly in fabric softeners but also in liquid detergents. The fundamental properties of silicones behind this application benefit are their low surface tension, low intermolecular interactions, high spreading and nonadhesive characteristics. Some studies have demonstrated high levels of silicone deposition onto fabric when delivered from fabric softeners.

Fabric Dewatering. There is an interest in terms of consumer convenience to accelerate fabric drying, matching wash and drying cycle times, and also to contribute to a reduction of electricity consumption when tumble dryers are used. Reducing the amount of water left in the fabric after the wash and spin cycle directly correlates with a reduction of drying time and energy. Studies have shown that when dosed at 1% active silicone in the softener, up to a 13% further reduction of water content can be achieved with the tested silicones over fabric rinsed with organic quaternary ammonium salts, which already reduce water content by 23% over the water-rinsed fabric. It is believed that the fundamental silicone properties behind this benefit are hydrophobisation of the fabric surface and its subsequent dewetting, as well as its low surface tension, which allows fast spreading. Several patents were issued and are commercially practiced [32-33].

Ease of Ironing. The ease of ironing benefit can be subjectively assessed through paired comparison panel tests but can also be objectively measured by coefficient of friction measurements. Several patents exist and are practiced in the fabric softener market [34-35]. The fundamental properties behind this application benefit are the same as softening, with the proviso of higher levels and external deposition of the silicone.

Wrinkle-Related Benefits. Perhaps the most critical objective of fabric care is to reduce garment wrinkling after the wash cycle and during ironing, and also to improve wrinkle resistance during wear. This is a difficult technical challenge, because the mechanism of wrinkle formation is complex and not easy to access from a laundry application perspective. The textile industry has been able to meet this challenge to some extent through the application of “easy care” finishes. These treatments are based on a high-temperature cure of crease resist resins (dimethylol-dihydroxyethyleneurea or DMDHEU), organic quaternary ammonium salts and silicones. However, this is not compatible with consumer washing processes and safety. The current opportunity is great for technical improvements that would bring satisfactory performance. Many patents [36-37-38-39] have been published in this field for various product formats (e.g., sprays, fabric softeners and detergents), and they always combine silicone with other ingredients or polymers. It is suspected at this stage that fibre lubrication is most likely to be the added benefit in this process together with the silicone softening touch.

Water absorbency. Fabric softeners have the down side effect of hydrophobizing fabric. This is a concern for consumers who want a soft, bulky towel with good absorbing properties. Surprisingly, in the middle 1980s, it was found that the addition of silicone polymer in a fabric conditioner composition actually improves the water absorbency of the fabric. Water absorbency is evaluated by a Drave’s wetting test, which measures the time required for a fabric sample to sink to the bottom of a 1 l beaker filled with demineralised water. Measurements are relative to a given organic quaternary ammonium salt type and are arbitrarily stopped after 300 s.

Several patents [40] were issued from the mid 80s until recently for a variety of silicone structures and compositions, but so far no clear, convincing interpretation of this phenomenon has been proposed. Because low molecular weight PDMS is known to be

the most effective in water absorbency studies, we suspect that the versatile orientation of the silicone molecule and its ability to modify surface hydrophobicity/hydrophilicity as well as its low viscosity and high spreading rate are involved.

Modification of the Mechanical Properties of Fabric. Sophisticated investigation found that particular silicone products formulated in a fabric softener have a positive impact on the fabric's mechanical strength compared to water-rinsed or pure softener-rinsed fabric. This was observed using the "tear crack propagation" method as described in the DIN ISO 13937-1:2000 standard. It is suspected that the elastomeric nature of the silicone polymer and its lubrication properties are involved in this phenomenon. It is also believed that treating fabric with silicone lubricants can reduce fabric wear abrasion and consequently improve color definition, reduce pilling and fuzziness, and help retain original fabric shape.

Silicones as Perfume Release Modifiers. Perfumes are present in almost all consumer surfactant-based products in the household and cleaning segments. Perfumes are added to cover residual odours from raw materials but also for more subjective purposes. Both protection and controlled release of perfumes have been areas of development in recent years in household and cleaning products. Silicones are being considered here because of their high permeability to gas and low molecular weight organic molecules and also because this property can be reduced and adjusted (e.g., by using bulky alkyl side groups). Silicone can also easily be formulated under different product forms: from volatile dispersions, emulsions, or particles to devices made from a cured elastomer [41-42-43-44-45].

7. Silicones in Coatings

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Silicones are widely used in the coating industries as materials to protect and preserve but also to bring style to a wide variety of applications in our daily lives.

The unique combination of properties of silicones is well suited to coating applications. Two families of products are used: silicone polymers as additives and silicone resins as the main component, or binder.

At low levels, silicone polymers are used to ease application of paints. The surface properties of silicones enable a paint to wet a substrate easily and give it a smooth appearance once dry. Here silicones are behaving as performance enhancing additives during the coating application. They are effective at an addition level of a fraction of a percent (see Table 4).

In contrast to the low-level use of silicone polymers as additives, silicone resins can be major components of the coating. Here they are used as binders or co-binders, imparting

important benefits such as durability throughout the life of the coating. Silicone resins offer resistance to weathering in paints for exterior surfaces such as bridges and metal cladding on buildings. They also provide water repellence to masonry surfaces such as stone and brick.

Silicone resins have greater resistance to high temperatures than organic resins and are used in paints for ovens, chimneys, car exhausts and barbecues. In these examples, the resilience of the silicone materials allows reduced frequency of maintenance painting and consequently reduced volumes of paint used over the lifetime of the coated item (see Table 4).

Table 4. Silicones in Coatings and Associated Benefits

<i>Silicone as performance-enhancing additives</i> (0.1 – 5.0 % w/w)	<i>Silicone resins and intermediates</i> (30 – 100 % w/w)
Foam control Substrate wetting Leveling Adhesion Surface slip	Weather resistance Heat resistance

Silicones as Performance-Enhancing Additives

Polydimethylsiloxane (PDMS) fluids of low-to-medium viscosity were the first silicone additives to be used in coatings. They readily dissolve in solvent-borne paints, reducing the surface tension of the liquid and enabling it to wet substrates, even if contaminated with dust, grease or oil. This reduces the appearance of film defects known commonly as “fisheyes” and “pinholes.” The silicone also reduces surface tension gradients across the coating film as it dries so a smooth surface is obtained rather than the undesirable “orange peel” effect.

Silicone polymers can be modified by grafting polyether groups to give silicone-polyether copolymers. These behave as surfactants in aqueous media as they have both hydrophobic and hydrophilic components. Such surface active materials can perform many functions in inks, paints and coatings. The main uses of silicone surfactants are to provide defoaming, deaerating, improved substrate wetting, and enhanced slip properties [46].

Silicone-polyethers are usually obtained by a platinum-catalyzed addition reaction of an unsaturated polyether onto a SiH functional silicone polymer (see Section 1). Therefore very many structures are possible, altering the SiH functional silicone polymer (DP, % SiH) and/or the nature of the unsaturated polyether (DP, unit type) (see Figure 7).

silanol-functional silicone resin intermediates were developed which could be reacted with hydroxyl-functional organic resins to give even greater weather resistance. Chemically combining the silicone and organic resins gives a higher degree of compatibility, allowing a broader range of organic resins to be used.

A comparison of the bond strengths between atoms that compose silicones and their organic counterparts gives some insight into why the silicone backbone is so robust when exposed to energetic conditions such as UV radiation or heat (see Table 5).

Table 5. Bond Strengths for Some Common Combinations of Atoms in Coating Resins

<i>Bond</i>	<i>Bond strength kJ/mol</i>
Si – O	445
C – C	346
C – O	358
Si – C	306

The Si-O bond has about 50% ionic character as calculated from Pauling's electronegativity scale. In aqueous media, Si-O bonds are more susceptible to hydrolysis than C-C bonds, especially in the presence of an acid or base. This might suggest that silicones would be expected to show less resistance to weathering than organic resins. The reason that this is not so is because the products of hydrolysis, silanol groups, rapidly condense to reform the silicone linkage (see Section 8). Moreover, the silicone hydrophobicity limits wetting and surface contact with any water-based media. However, water vapor can diffuse through most silicone polymer coatings, which is advantageous in some applications like masonry treatment.

Typical silicone resin intermediates used in solvent-borne alkyd or acrylic resin paints are oligomeric materials including T units (see Section 1) with phenyl and propyl groups to improve their compatibility. They have some Si-OH or silanol groups that can be condensed with C-OH or carbinol groups of the alkyd or acrylic resin (see Figure 8).

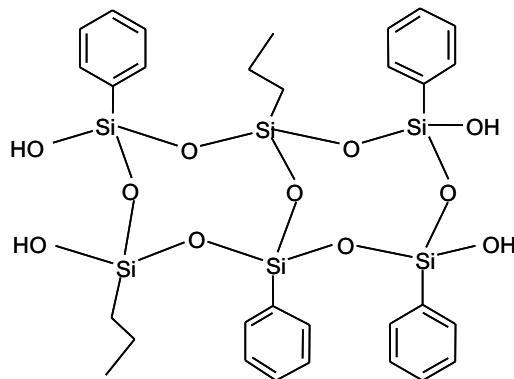


Figure 8. A phenyl-, propyl-functional silicone intermediate used to modify organic resins (idealised structure).

These silicone-organic copolymers are used in industrial maintenance paints to protect a variety of metal objects and structures, including railway carriages, chemical plants and bridges. The biggest application in the US is the painting of naval ships according to specifications set by the federal government. Periods between recoating were extended from a maximum of one year for straight alkyds to three years for the silicone-modified versions. A typical silicone-alkyd copolymer for this type of paint contains 30% silicone based on resin solids.

The success of silicone-alkyds in naval applications led to the evaluation of silicone-organic copolymers in coil coatings for residential and commercial aluminium sidings. As these coatings can be cured at elevated temperatures, silicone-polyesters without drying oils were found to be most appropriate. At first, a 50% silicone content was the standard based on accelerated weathering data, but as more field experience was gained it became apparent that 30% silicone is sufficient.

Solvent-borne thermoplastic acrylic resins tend to have better chemical resistance than alkyds and can be cold blended with silicone resins to give weather-resistant paints for exterior applications. Addition of as little as 10% silicone can significantly increase the gloss retention and chalking resistance. The improvement that can be achieved in gloss retention of various organic coating resins through silicone modification is illustrated in Figure 9 [49].

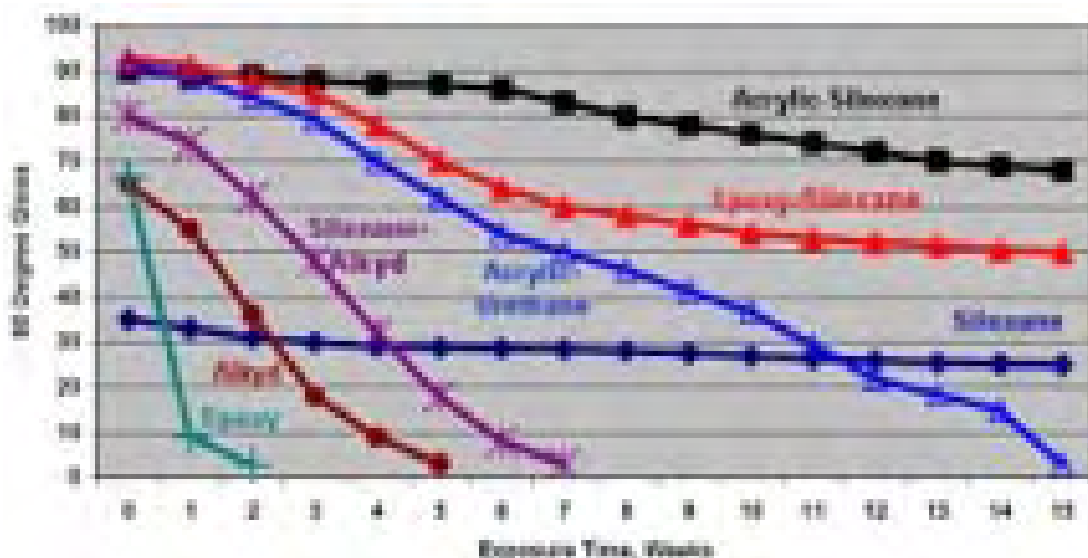


Figure 9. Gloss retention of coatings made from organic resins and silicone-organic combinations; QUV-B accelerated weathering.

The modification of acrylic latexes (water-borne formulations) with silicones is proving to be an effective way to comply with regulatory restrictions on solvent use. Combinations of monomeric silicon intermediates with alkoxy functionality can be blended with hydroxyl functional acrylic latexes to give silicone-acrylic copolymers with excellent weather resistance. The ratio of alkyl- and aryl-bearing silicon monomers can be

optimized to give the best balance of compatibility, film flexibility and durability. Gloss retention of paints formulated from acrylic latex with 10% modification is typically 50 to 70% after 30 months of south Florida exposure, compared to about 10% for the unmodified latex.

Silicone Resins in High Temperature Paints

Silicone polymers or resins can be regarded as already partially oxidized as they consist partially of Si-O groups. This is one of the reasons for the high thermal stability of silicones compared to organic materials. The bond strengths in Table 5 provide additional explanation of the observed stability.

Phenyl groups attached to silicon are far more resistant to thermal oxidation than methyl groups. So, most silicone resins for high temperature applications have a combination of methyl and phenyl substituents to achieve the required balance of heat stability, flexibility and compatibility with organic resins.

Blends of silicone and organic resins are suitable for applications up to about 400 °C. The proportion of silicone required increases vs. the expected upper operating temperature, as observed with the effect of adding a methyl/phenyl silicone resin into an alkyd paint exposed to various temperatures (see Figure 10) [50].

For temperatures above 400 °C, silicone resins are used only as binders. These can be formulated with aluminum pigments to form a ceramic film as the silicone organic substituents are burned off to give a very durable fully oxidized siliceous layer.

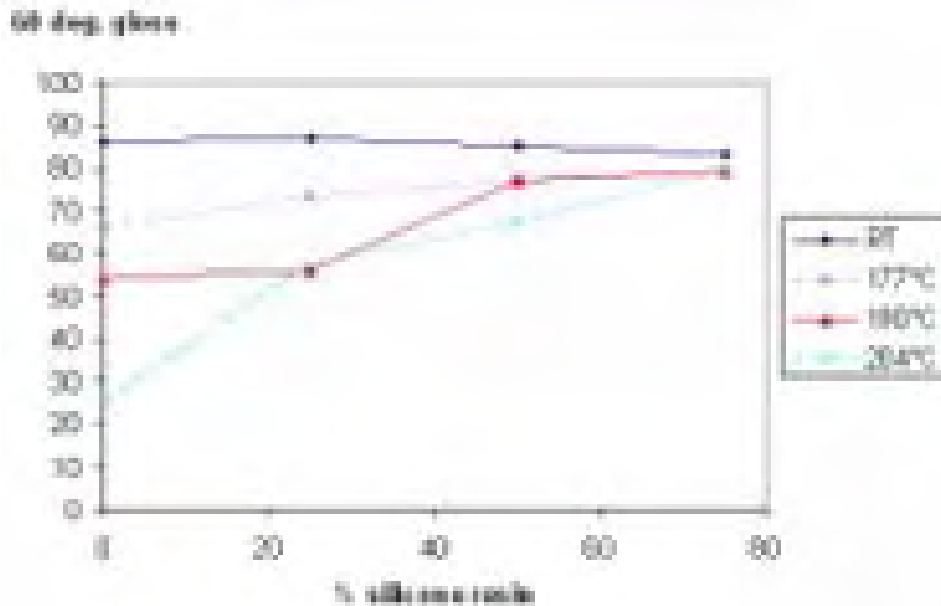


Figure 10. 60° gloss vs. methyl/phenyl silicone resin content in an alkyd paint based on nondrying coconut oil after 16 hours exposure at different temperatures.

Silicones for Marine Fouling Release Coatings

Solid surfaces immersed in seawater quickly become covered with algae, barnacles, tubeworms and other marine organisms. On ships this is referred to as fouling, which increases drag on the hull and raises fuel consumption by up to 40%. To prevent this, antifouling coatings are applied to the hulls. The most effective coatings were based on organo-tin compounds, and in the 1970s, 80% of the world's shipping fleet had this type of coating. Environmental concerns have motivated many countries to ban organo-tin coatings. So considerable research and development is taking place in government agencies and paint companies to find alternatives. Silicones have been identified as critical materials.

A typical silicone-based anti-fouling/release system consists of an epoxy or silane primer, an elastomeric silicone tie-coat and an elastomeric silicone top-coat that contains a release additive. The release additive must have limited compatibility with the coating so it will migrate to the surface. Organic oils and waxes have been shown to work as release additives, but the most effective materials are modified silicone polymers with a combination of methyl and phenyl substituents. The latter reduce the compatibility of the polymer with the predominantly PDMS network of the elastomeric coating. Figure 11 shows a system of this type applied to a test panel and immersed in the English Channel for two-and-a-half years. The panel is almost completely free of fouling organisms. Surprisingly, a comparison coating based on PTFE, which has also a very low surface energy, is completely covered. This indicates that a coating with a low surface energy is not a sufficient requirement for effective fouling release. The inclusion of a release additive, as in the silicone elastomeric system, has a dramatic and positive effect on performance.



Figure 11. *Extent of fouling of coated steel panels submerged for two-and-a-half years in the English Channel. Picture courtesy Dow Corning Ltd.*

The ban on tin-containing anti-fouling coatings for marine applications has opened up an area that is surely a logical fit for silicone technology. This may well be the largest “release” application in the world, release being a function that silicones have provided for many years in bakeware, mold-making and adhesive label backing paper.

8. Silicones in the Construction Industry

A. Wolf, Dow Corning GmbH, Wiesbaden (Germany)

Silicone sealants and adhesives as used in the construction industry were introduced approximately forty years ago, and many of the silicones applied in the early days are still performing today. Products are available in a variety of forms, from paste-like materials to flowable adhesives. Both single- and multi-component versions are available, each with several different cure chemistries.

The commercial importance of silicone sealants and adhesives is based on their unique combination of properties that permit them to satisfy important needs in a broad variety of markets. These properties include excellent weather and thermal stability, ozone and oxidation resistance, extreme low temperature flexibility, high gas permeability, good electrical properties, physiological inertness and curability by a variety of methods at both elevated and ambient temperatures. Because of their low surface energy, they wet most substrates, even under difficult conditions, and when formulated with suitable adhesion promoters, they exhibit very good adhesion. These unique characteristics are the result of a scientific endeavour to combine some of the most stable chemical and physical attributes of the inorganic world with the highly utilizable aspects of organic materials.

A qualitative list of the features of siloxane polymers that contribute to the unique combination of properties of silicone sealants and adhesives relevant in construction applications is given in Table 6. Almost all these inherent attributes are a consequence of four fundamental aspects: the low intermolecular forces between dialkylsiloxane molecules, the dipolar nature and the strength of the siloxane bond and the flexibility of the siloxane backbone.

Probably the most important properties of silicone sealants for construction are durability and adhesion.

Table 6. Silicone Attributes Contributing to Durability

<i>Sealant Property</i>	<i>Silicone Attribute</i>
Excellent substrate wetting (adhesion)	Low surface tension
High water repellence	Low surface tension
Excellent flexibility	Low glass transition temperature Large free volume Low apparent energy of activation for viscous flow Low activation energy of Si-O-Si bond rotation
Small temperature variation of physical properties	Configuration of siloxane polymer chain and small interaction between methyl groups Low activation energy of Si-O-Si bond rotation
Low reactivity	Configuration of siloxane polymer chain and small interaction between methyl groups
High gas permeability	Large free volume Low activation energy of Si-O-Si bond rotation
High thermal and oxidative stability	High Si-methyl bond energy
Ultraviolet light resistance	High Si-O bond energy

Adhesion

Although the primary function of sealants is to seal, in most applications they cannot provide this function without proper and durable adhesion to the substrate(s). Furthermore, in many applications, it is difficult to distinguish between an adhesive and a sealant. For example, structural silicone adhesives are used in the building construction industry owing to their sealing, adhesive and elastomeric properties, as well as their resistance to harsh environmental conditions.

The type of application dictates the adhesion requirements. For instance, sealants and adhesives for general use are expected to achieve primerless adhesion to a broad variety of substrates.

Siloxane polymers spread easily on most surfaces as their surface tensions are less than the critical surface tensions of most substrates. This thermodynamically driven property ensures that surface irregularities and pores are filled with sealant or adhesive, giving an interfacial phase that is continuous and without voids. Thus, maximum van der Waals and London dispersion intermolecular interactions are obtained at the silicone-substrate interface. However, these initial interactions are purely physical in nature. Theoretically, these physical intermolecular interactions would provide adhesion energy on the order of several mJ/m^2 . This would be sufficient to provide some basic adhesion between the adhesive and the substrate. However, the energy of adhesion required in many applications is on the order of kJ/m^2 . Therefore, physical intermolecular forces across the interphase are not sufficient to sustain a high stress under severe environmental conditions. However, chemisorption also plays an important role in the adhesion of

reactive silicone sealants and adhesives; thus, physisorption and chemisorption both account for bond strength [51].

Obviously, the ideal silicone adhesive or sealant is one that is self-priming; that is, the adhesion promoter is included in the formulation and is generally part of the curing reaction system. This is the most common type of commercial silicone sealant or adhesive, as it often provides adhesion without the need of a complicated pretreatment procedure such as priming, corona- or plasma-treatment. However, even with self-priming systems, proper cleaning of the substrate prior to application is required to eliminate weak boundary layers and to achieve strong and durable adhesion.

Durability

Properly formulated silicone sealants and adhesives exhibit outstanding durability in a variety of environments. They are known for their high movement capability; their excellent resistance to ultraviolet light, high temperature and ozone; their low water absorption and low temperature flexibility, as well as their ability to form strong chemical bonds to the surface of typical construction and industrial substrates [52]. The outstanding UV stability of silicones is derived from the bond strength of the silicon-oxygen linkages in the polymer chain, as well as the absence of any double-bond or other ultraviolet (UV) light-absorbing groups.

The principal environmental factors acting on a sealant or adhesive in outdoor exposures are:

- Temperature extremes (high and low)
- Water
- Solar radiation (UV and IR)
- Oxygen/ozone
- Corrosive gases (sulphur dioxide, nitrogen oxides)
- Mechanical stress

For radiation energy to initiate chemical changes, the molecules of the material in question must absorb it. Silicones absorb very little ultraviolet radiation in the 300-400 nm region, which is the wavelength range that causes problems with most other polymers at, or near, ground level. When irradiated under conditions of natural photo-aging, silicones are slowly oxidised. The oxidation of the hydrocarbon side-groups results in the formation of carbonyl groups [53-54-55-56]. Since carbonyl groups do not interact strongly, the oxidation has little effect on the mechanical properties of the sealant or adhesive. This is consistent with the fact that, even after 20 years of outdoor weathering in sunny climates, silicone elastomers show comparatively little change in physical properties [57-58].

Under natural weathering conditions, the effects of oxygen and ozone are inextricably connected to those of elevated temperatures and sunlight. At room temperature, oxidation by oxygen is not noticeable. The excellent oxidation resistance of silicones is a consequence of the dipolar character of the siloxane backbone. The positively polarised silicon atom acts as an electron drain for the methyl group, rendering it less susceptible to

oxidation [59]. Oxidation in air generally becomes noticeable above 200°C, resulting in cleavage of the Si-C bond. However, one can raise the upper service temperature by using suitable oxidation inhibitors.

Changes in the physical properties of silicones under artificial or natural weathering conditions, involving alternating periods of wet and dry conditions, are mainly due to the physical effects of water [60]. Since the hydrolysis reaction is reversible, some of the siloxane bonds that were ruptured by hydrolysis are formed again by the condensation of silanol groups upon drying [61]. Thus, during alternating periods of wet and dry conditions, a relatively small number of siloxane bonds in the bulk of the sealant or adhesive are constantly broken and reformed.

Silicone sealants and adhesives show excellent resistance to the combined effect of the key weathering factors: water, heat and ultraviolet light [62-63]. Compared to organic sealants and adhesives, silicones are more thermally stable, perform over a wider range of temperatures, have a higher movement capability and are less susceptible to fatigue resulting from cyclic mechanical strain. They are also more resistant to UV light as well as oxygen and ozone attack. They are also known for their low water absorption and the ability to form strong chemical bonds to typical construction substrates.

A weaker aspect of the environmental stability of silicones is their susceptibility to hydrolysis reactions, particularly at the extremes of acidity or alkalinity and at elevated temperatures. Exposure to strong acids and bases as well as to super-heated steam are detrimental to the stability of silicone sealants. Under natural weathering conditions (involving small amounts of water incorporated in the bulk of the sealant or adhesive), mass action effects keep the hydrolysis reaction within limits, a condition much aided by the low water wettability of the siloxane polymer.

Applications

The construction industry represents the largest market segment for silicones. Silicone sealants, primarily as one-part room temperature vulcanisable (RTV) products, are widely used by the construction industry for applications such as sealing building and highway expansion joints, general weatherproofing of joints in porous and nonporous substrates, sanitary joints around bathroom and kitchen fixtures, as well as fire-rated joints around pipes, electrical conduits, ducts, and electrical wiring within building walls and ceilings. In a variety of applications, silicone sealants also perform the functions of an adhesive (i.e., they act as structural sealants). For example, silicones are used in structural glazing, where the cured sealant becomes part of the overall load-bearing design, or in insulating glass secondary seals, which structurally bond two panes of glass together. Structural glazing is the application that most importantly is enabled by the outstanding durability of silicone sealants.

Structural silicone glazing (SSG) is the method of bonding glass, ceramic, metal, stone or composite panels to the frame of a building by using the bond strength, movement capability and durability of a silicone structural sealant. Figure 12 shows the Burj-Al-

Arab hotel in Dubai as one example of the many exceptionally well-designed buildings sporting silicone structural glazing façades.



Figure 12. *Burj-Al-Arab Hotel, Dubai; a tribute to the use of structural glazing silicone adhesive in a high-rise façade.*

Because of the elastomeric character and the chemical adhesion of silicone structural bonding seals, SSG design concepts offer a number of performance benefits [64]:

- Effective air- and weather-sealing of the façade
- Improved thermal and sound insulation
- Protection of the supporting structure from the elements by a durable glass skin
- Increased rigidity and stability of the façade, resulting in the ability to withstand higher wind-loads
- Ability to absorb differential movements between glass and building frame, resulting in superior performance of SSG façades during seismic events

For the façade designer, SSG provides the possibility to construct façades with free-flowing, uninterrupted bands of glass or smooth, uninterrupted total glass surfaces.

The SSG technique uses both the adhesive and sealing properties of structural silicone sealants. Medium modulus, good elastomeric properties, and excellent, highly durable adhesion are important to support the weight of glazed panels and to resist wind load, while simultaneously being able to absorb differential movements between dissimilar materials induced by thermal fluctuations, seismic loading or other forces. It is essential for the success of SSG design to use a structural sealant and not a rigid adhesive because

the structural seal needs to resist both loads and movements without creating unduly high stresses at the glass interface or failing cohesively [65]. Since the interface between structural seal and glass is directly exposed to sunlight, the sealant must develop extremely UV-stable bonds to the glass substrate to achieve an expected service life of 30 to 50 years. Because of this requirement, only silicone sealants are allowed for structural glazing applications.

9. Silicone Release Coatings for the Pressure Sensitive Adhesive Industry

S. Cray, Dow Corning Ltd, Barry (Wales)

In today's modern environment there is a wide range of applications for silicone release liners with pressure sensitive adhesives, ranging from release labels to diaper closures, medical applications (e.g., wound dressings), building insulation and health and beauty products [66-67-68].

Release liners are part of a composite made of a label with its own adhesive on a release liner or carrier with its own release coating. The label comprises either a synthetic face stock such as polypropylene or paper. The adhesive is usually an organic material such as a polyacrylate or polyisoprene based rubber. The release liner can be made from various substrates treated with a suitable product, the release coating. Such release liners allow transporting labels with their adhesives from the point of manufacture to the point of label application (e.g., a filling station of some sort). The release coating allows easy delamination or easy label transfer from their liners onto the object to be labeled.

The use of release liners began before World War II but really took off with the development of silicone release coatings in the early 1950s. There are several chemical types of release materials. However, many are migratory types; that is, significant amounts of the release material contaminate the surface of the released material. Those that do not migrate or transfer to the released material to any significant degree include polyacrylates, carbamates, polyolefins, fluorocarbons, chromium stearate complexes and silicones. Silicones enjoy a unique position because they can be applied and cured into a polydimethylsiloxane (PDMS) network on various backing substrates so limiting migration, but also because they allow substantially lower release forces than other materials. Silicone-coated substrates are sometimes referred to as siliconized release liners.

The choice and combination of backing substrate, silicone release coating and adhesive needs to be carefully selected.

Silicone Release Characteristics

One of the key properties of silicone is its low surface tension, and in particular, its low critical surface tension of wetting or low surface energy. This is a consequence of low

intermolecular forces and high chain flexibility (see Section 1) [69]. Unlike more rigid carbon-carbon backbones, PDMS polymers because of their backbone flexibility, and as they are at room temperature substantially above their T_g , can easily expose their low interacting/surface active methyl groups to provide low adhesion; or in other words, low release forces against adhesives they are exposed to.

Organic adhesives as used on labels cannot easily wet such a low energy silicone surface as there are no groups to interact, which results in ease of delamination and ease of transfer of the label from the liner to its point of use.

But low surface energy is not the only aspect to consider. Even fluorocarbons, despite a lower surface energy than silicones, do not match silicone release performance. Another key component is the rheological behaviour of the cured PDMS network applied onto the backing substrate [70]. Recent work has shown that interfacial slippage also plays a role in the low release values observed on the release of pressure sensitive adhesives from silicone release coated liners [71-72-73]. A mechanism has been proposed for cured PDMS network/release coatings in which interfacial slippage minimizes the bulk shear deformation experienced by the organic adhesive [73].

Commercially cured PDMS release coatings can exhibit significant interfacial slippage. Sometimes silicone resins known in the paper industry as release modifiers need to be added to a silicone formulation to increase release forces. This may be necessary for processing reasons to convert the laminate construction to the label, or it may depend on the release force required for particular dispensing application.

It is believed that these release modifiers “freeze out” interfacial slippage, resulting in increased adhesive deformation upon delamination and higher release forces. The release modifier reduces the segmental mobility of the PDMS chains within the cured coating network. If the PDMS is constrained by a rigid backing, there is still slippage at the interface due to bending of the PDMS at the crack tip at finite peel angles. It has become clear that the great advantage of PDMS in release applications is its low coefficient of friction under shear, compared to lower surface energy but higher shear friction (more rigid) fluorocarbons.

Factors to Consider for Silicone Release Coatings

Many other factors influence the selection of coating technologies and materials for liners and laminates. These include end-user requirements like converting, die-cutting and printing requirements and environmental concerns. If using silicones, some factors are related to them, some not (see Table 7).

The equipment used may drive the choice of release coating material. Most commonly used are either based on a three roll differential offset gravure or a five or six smooth roll coating head. Environmental and regulatory pressure may play a role as well, encouraging the selection of solventless or emulsion systems to deliver the required performance.

Substrate type, cure temperature, dwell time and humidity can affect cure and anchorage of the silicone coating to the substrate. The selection of adhesive required for the application also has a major bearing on release and anchorage characteristics.

In recent years, the use of plastic liners such as polyethylene, polypropylene or polyester films has increased. Siliconizing such substrates is a challenge because of their low resistance to high temperatures and their variability as they may contain additives such as antiblocking agents or stabilizers. Some of these are detrimental to the cross-linking of the silicone release coating. But overall these thermoplastic films are difficult substrates as they show poor adhesion and sometimes poor silicone cure to the applied coating. Special grades of film have been developed to improve adhesion, but they are more expensive. UV-cured silicone release coatings have been developed to avoid exposure to high curing temperatures, but overall the penetration of such UV-cured systems is low compared to heat-cured systems, which remain the preferred system.

If using silicone release coating materials, there is an array of silicone chemistries to select from. UV cure is sometimes used when applying a release coating on a low melting temperature substrate such as low density polyethylene [74], but the most widely used cured chemistry for silicone release liner preparation is thermal cure.

To achieve a cured network, there are solvent-based, emulsion-based and solventless silicone systems [75]. Whereas the coating of the first two types is relatively straightforward, the coating of 100% solids materials is highly specialized and needs sophisticated coating equipment.

Table 7. Factors to Consider When Using Silicone Release Coatings

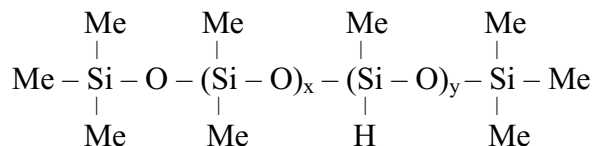
<i>Non silicone related factors</i>	<i>Silicone related factors</i>
Equipment	Silicone cure chemistry
Substrate	Composition:
Cure temperature	- polymer architecture
Dwell time	- modifier architecture
Humidity	- cross-linker architecture
Adhesive type	- additives

Cure Chemistry

To avoid migration, the PDMS release coating is applied and then heat cured onto the substrate to give a cross-linked silicone. To achieve cross-linking of the silicone release coating, the most predominantly used chemistry is cure via a hydrosilylation reaction. The composition of such silicone release coating consists of vinyl-functional PDMS, a hydrogen-functional PDMS and a platinum catalyst (see Figure 13). These can be reacted together using a hydrosilylation reaction. Additives used include inhibitors to provide for long bath life at room temperature and release modifiers. These silicone coatings are

formulated to achieve rapid cure when used and exposed to high temperature to achieve high coating speeds.

a) *hydrogen-functional siloxane*



b) *vinyl-functional siloxane*

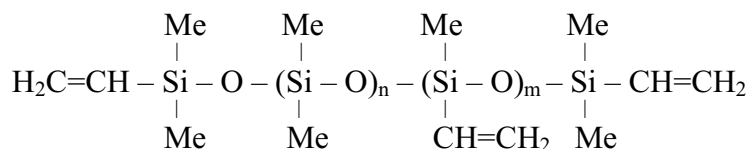


Figure 13. Structures of the silicone polymers used in release coatings.

The hydrosilylation reaction, especially of carbon-carbon multiple bonds, is one of the most important reactions in organosilicon chemistry and has been extensively studied for half a century [76-77-78]. This reaction is used to produce many organosilicon compounds. However, one of its primary uses is as a fast cross-linking or cure chemistry reaction as here to cure silicone release coatings.

Hydrosilylation is the addition reaction of a silane group (SiH) on a vinyl group (Si-CH=CH₂) catalyzed by a noble metal such as rhodium or most often platinum. A general model has been proposed to explain how the platinum is involved in the reaction (see Figure 14) [79]. There are basically two different forms of this cure chemistry used industrially, both catalyzed by platinum. In one, a SiH-functional polymer reacts with a vinyl-functional polymer carrying Si-CH=CH₂ groups. In the other, a SiH functional polymer reacts with a hexenyl functional polymer carrying Si-CH₂-CH₂-CH₂-CH₂-CH=CH₂ groups (see Figure 14).

This simplified proposed mechanism does not explain the difference between vinyl- and hexenyl-based systems. In the hexenyl-based system, the unsaturation has been distanced from the polymer backbone and is therefore less sterically hindered. This allows a release coating material with a slightly faster cure upon application.

Associated with these two different forms of cure chemistry (vinyl or hexenyl), various inhibitors can be used to ensure sufficient bath life and prevent premature cure at room temperature of the coating mixture prior to use and curing. Inhibitors compete with the initial step of the hydrosilylation reaction and the addition of the unsaturated group from the polymer on the platinum catalyst (see Figure 14). So the selection of the platinum inhibitor has a major impact on cure speed [80-81]. An inhibitor strongly bound to the

platinum catalyst forms essentially a very high barrier of access for the unsaturated group from the polymer to the active platinum catalyst center during stage one of the reaction mechanism above. Typical inhibitors employed here are acetylenic alcohols such as 1-ethynyl,1-cyclohexanol or fumarate- or maleate-based inhibitors.

As the price of platinum increases (it has doubled in recent years), new polymer/cross-linker structures have been developed to reduce costs, in particular for solventless coating. Today rapid cure can be achieved with lower levels of platinum (i.e., 50 instead of 100 ppm).

As line speeds increase, the silicone is submitted between applicators at the nip of the coating equipment and the substrate to shear rates of the order of 10^6 sec^{-1} . At these high shear rates, the silicone behaves very differently than expectations based on rheological measurements, which are usually made under relatively low shear. Silicone misting is one such manifestation [82-83]. So additives have been developed that will greatly reduce the volume of mist produced, even at 1600 m/min [84].

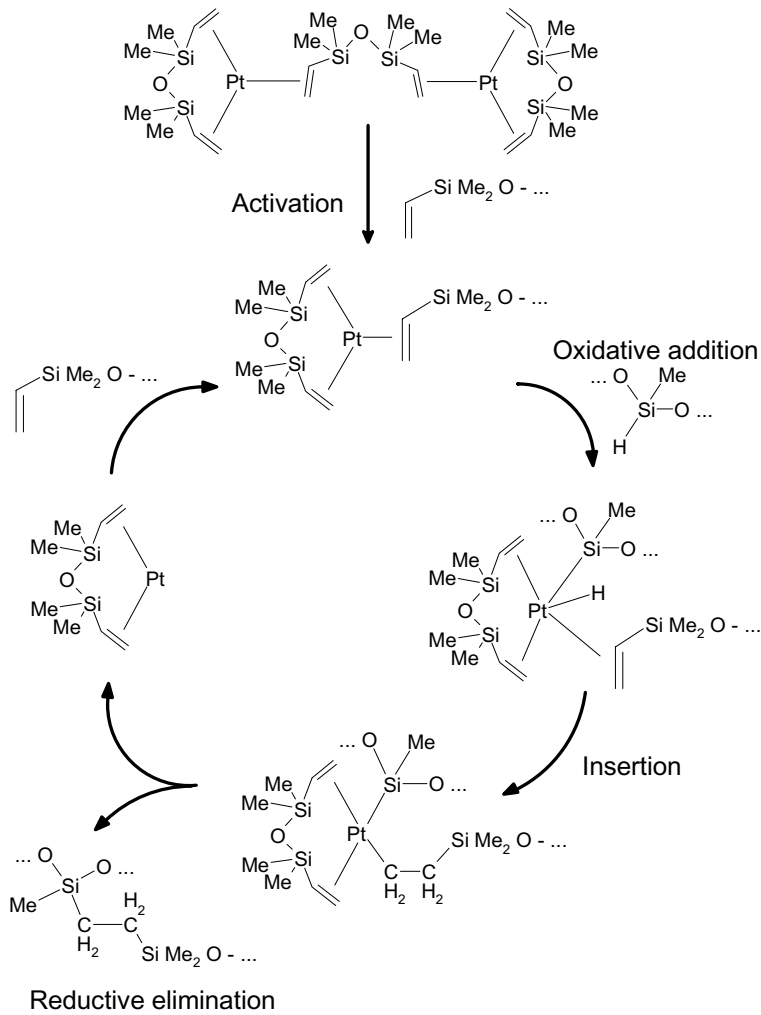


Figure 14. *Hydrosilylation/addition cross-linking and cure mechanism.*

Greater Use of Plastic Release Liners

In recent years, the use of plastic release liners such as polypropylene, polyethylene and polyester has increased, fueled in part by an increase in premium applications such as no-label-look beverage labels for aesthetic appeal and brand enhancement.

The siliconising of plastic films has a number of associated problems. These include the requirement of low curing temperature for polyolefin films, amongst others. Further, there is difficulty in adhering silicones to plastic films and maintaining anchorage of the silicone to the plastic film over time. This problem is particularly prevalent with polyester films. In addition, plastic films are quite variable. For example, several additives can be used in film production including antiblocking agents, heat stabilizers and plasticisers. These additives can affect cure and anchorage. This variability adds to the design complexity for a robust universal thermally-cured silicone system.

Some of the cure and anchorage issues associated with some plastic films can be overcome by using special grades of film. For example, co-extruded or primed polyester is used to ensure that there is no adhesion failure of the silicone to the film over time. However, these special grades of film are generally more expensive than standard grades. Consequently, the widespread use of these "treated" films has been limited.

The challenges to the silicone supplier are to develop robust silicone release coating systems for general grades of film that overcome the problems discussed above. The first attempts to overcome some of the challenges of coating films were made with the introduction of UV-curing silicone systems. UV-curing silicone systems met the low temperature constraints for polyolefin films. However, due to customer preferences and all-round release performance, thermally-curing silicone release coating systems that provide robust performance to films have been sought.

10. Silicones as Mold-Making Elastomers

A. Colas, A., Dow Corning Europe SA, Seneffe (Belgium)

Long ago, people must have realised that clay could be used to take imprints of simple objects like a leaf, or later, a coin. Carefully withdrawing the clay gave a negative of the object or a mold in which other materials like plaster could be cast to reproduce the original. Clay is still used today to make molds, particularly to reproduce museum pieces like statues, not only because it is inexpensive, but also because clay is water washable and unlikely to contaminate or stain any valuable and unique original.

Clay molds are made by applying a layer of clay a few centimetres thick, and not too wet, on the original coated with talc. The clay is covered with plaster to provide a rigid backing or counter mold. A fine metallic wire can be laid onto the original surface before applying the clay to help dismantling. This allows the clay mold to be split neatly in smaller parts. If needed, the original is copied in many pieces. After re-assembling the

mold and its backing, plaster can be used to fill the clay mold to make copies and disseminate an object that otherwise would be unique and could only be seen by a few. “Does it matter that a copy is being shown and exposed?” the question has been asked. Providing that the copy is properly finished, all the artist's original work will be visually as present in the copy as in the original. So much so, that copies have been stolen from museum displays!

Yet the above technique suffers some shortcomings. Clay does not perfectly wet the original, and details are not perfectly captured. Seals between mold parts are difficult to make, leading to visible imperfections in the copies. The poor recovery after deformation or the clay's plastic nature creates distortions upon demolding. And such clay molds may be good for making only one copy.

A major improvement was found with the use of elastomers as mold-making materials. These mold-making elastomers are supplied as liquid compositions, usually two-part materials, and are easy to cast around the original. After hardening, they set into a flexible material that can be stretched to ease demolding, even around deep undercuts. However, because of their elastomeric nature, they return to their original shape to give a cavity containing in negative all details of the original surface.

The first reference about the use of silicone molds appeared in the 50s. Mention is made of a composite made of mica or paper and a binder, and shaped around an electrical coil using a silicone mold [85]. The earliest true mold-making application with silicones, where the details of the original surface are being transferred via the mold, appears to be in dental molds, with commercial products available from 1955, and fast-curing compositions later [86].

Compared to molds made of metal and where a cavity must be created with all the details of the desired finished object in negative, elastomers used as mold-making material require little tooling, providing an original object exists and from which a mold can be made. Metal molds perform well when many copies are needed. Molds made from an elastomer are an interesting alternative for short-copy series.

Process Description

Different elastomer products are available to prepare molds. Their common and key feature is that they are initially fluid compositions that can be poured around the original before hardening into a solid elastomer. This transformation is obtained by cooling for a thermoplastic elastomer, by water evaporation for a latex emulsion or by a chemical reaction for a two-part reactive system.

The simplest mold is known as the one-piece block mold (see Figure 15):

- The original, master or model is fixed into a container or countermold with appropriate clearance left all around
- After processing of the mold-making elastomer material (melting or mixing), the liquid composition is poured in the space between the original and the countermold

- After hardening and disassembling, a one-piece elastomer block mold is obtained whose internal surface contains in negative all the details of the original.

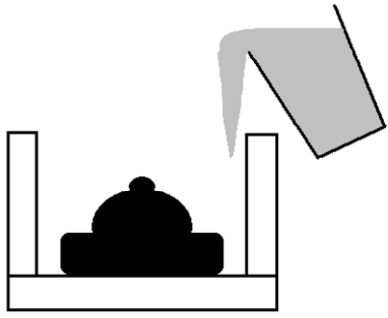




<p>Step 1: Fix the original in its counter-mould; apply a release agent; cast the two-part silicone elastomer after mixing and de-airing the two-part mixture.</p>		<p>Step 2: Allow the two-part silicone elastomer mixture to cure to an elastomer.</p>	
			
<p>Step 3: Dismantle to obtain the one-piece block mould.</p>		<p>Step 4: Cast a suitable copying material (plaster or resin).</p>	<p>Step 5: Dismantle to obtain the copy.</p>
			

Figure 15. Process steps for making a one-piece silicone elastomer block mold (original in black, counter-mould in white; two-part silicone elastomer mixture and cured silicone mold in light gray; copy in dark gray).

This one-piece block mold can now be used to cast plaster, polyester or any other suitable material to obtain positive copies of the original (see Figure 16).



Figure 16. Flexible one-piece block molds: a silicone mold being separated from a PU copy (left); a silicone mold, and two copies, one after and one before finishing (right). Pictures courtesy of Dow Corning.

But more complex molds are also used. A three-dimensional original (e.g., a statue) can be copied with a mold of two or more pieces (i.e., to render both front and back surfaces, which a simple block mold cannot do). In contrast, skin molds can be used for very large originals that are rather “flat” (e.g., a cathedral door). In this case, the object can be copied with only a thin layer of a thixotropic mold-making material to limit the amount of material used and reduce costs. Here thixotropy can be induced with additives like glycols or silicone polyethers capable of interacting with filler particles present as reinforcing fillers and by hydrogen bonding to give a nonflowing molding material. Such skin molds carry all the details of the original surface but are not self supporting like a block mold. A suitable countermold, usually made of fiberglass-reinforced polyester, must be built directly on top of the skin mold after the mold-making material has hardened.

So, most complex molds are made of many pieces, each of the skin type. Less elastomer is used, but more time is spent preparing the original; that is, hiding or masking some parts of it with clay or plastiline to mold only part of the original surface at a time (see Figure 17).

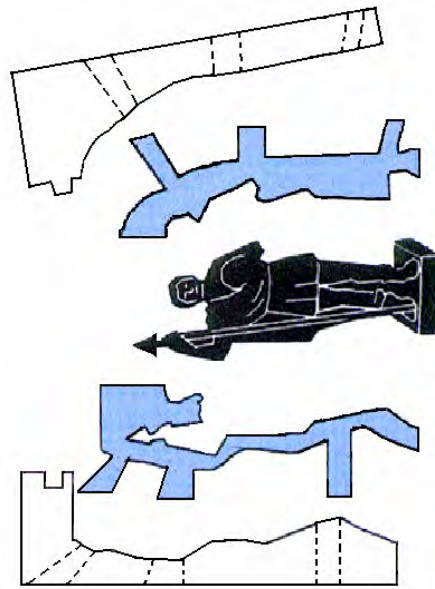


Figure 17. *A complex mold made of two skin pieces (in blue), each with its own supporting countermold (in white) around the original (in black). Protuberances are designed to ensure that the skins adjust properly to their respective countermold parts.*

Mold-Making Elastomers

Various elastomeric materials are used as mold-making material:

- Thermoplastic, like plasticized PVC, is inexpensive, but the original must allow exposure to high temperatures from the hot melted mold-making material
- Latex-based emulsions of limited stability upon shelf aging or against the heat generated by some copying resins (see further)
- Two-part silicone elastomers

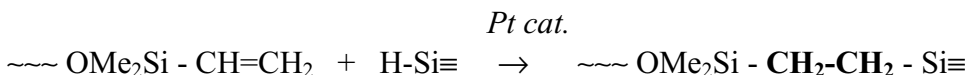
Two-part silicone elastomers have distinctive advantages:

- They are available as two-part materials; that is, as two components to be mixed just prior to use in a fixed ratio such as 10:1 or 1:1 to give a liquid mixture that can be poured or plastered around the original
- Their low surface tension allows them to pick up minute details from the original surface
- They harden, cure or cross-link into high-strength elastomers at room temperature without exotherm, and so do not expose the original to thermal stress
- Because of their low surface energy, various casting materials can be used to make copies without the risk of adhering to the silicone surface; because of the silicone heat stability, resins with strong exotherms can be used

Two-Part Silicone Mold-Making Elastomers

PDMS polymers are liquid at room temperature, even those of very high molecular weight. Their low T_g and the flexibility of their backbone make PDMS materials ideal candidates for formulating elastomers. A chemical reaction is yet required to attach or connect the free-flowing PDMS chains to form a solid, three-dimensional network or an elastomer capable of sustaining mechanical deformations. To allow for this, groups that can be reacted between polymer chains via a cross-linker in presence of a suitable catalyst must be present on the silicone polymer chains. Two different cross-linking systems have been developed, referred to as addition cure or condensation cure.

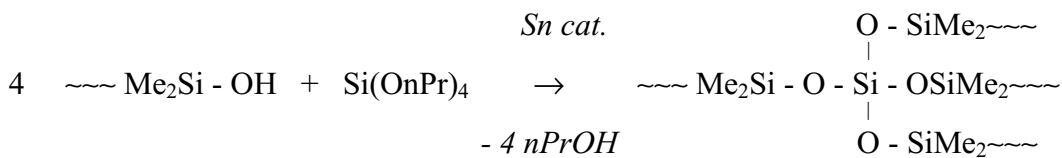
The addition cure is based on vinyl end-blocked PDMS polymers that are cross-linked by a SiH functional PDMS oligomer using a platinum-based catalyst, according to:



where $\sim\sim\sim$ represents the remaining part of the PDMS chain.

If the SiH functional PDMS contains three or more SiH reactive groups, many PDMS chains can be linked together to form a three-dimensional network. This reaction is an addition cure reaction, and no byproducts are evolved. So molds made using this reaction do not show shrinkage (see further). A platinum-based catalyst is used here and is prone to inhibition problems. Platinum catalysts work because they can bind to the weak electron-donating vinyl groups of the polymer chains (see Section 9). But, if better electron-donating groups are available in the vicinity (e.g., amine or sulphide), these can permanently bind with the platinum catalyst and completely inhibit its activity. Such impurities may come from nearby tools such as sulphur-vulcanized rubber gloves or from the original surface. When encountered, inhibition keeps the two-part addition cure elastomer from cross-linking properly, and it may badly stain the original (a small trial in a nonconspicuous place is recommended).

The condensation cure is based on hydroxy end-blocked PDMS polymers that are cross-linked by an alkoxy silane in presence of a tin catalyst according to:



where $\sim\sim\sim$ represents the remaining part of the PDMS chains.

Alcohol is evolved during cure, resulting in some material loss and shrinkage (up to 2% linear shrinkage). Molds made using this reaction will not perfectly respect the dimensions of the original. But this reaction is not prone to inhibition except in very rare cases [87].

Advantages and limitations of both addition and condensation cure or cross-linking systems are summarized in Table 8.

Table 8. Comparison of the Properties of Addition and Condensation Cure Silicone Two-Part Mold Making Elastomers

	Addition cure	Condensation cure
Inhibition	Possible	Very rare
Shrinkage (% linear)	Low (< 0.1)	Medium – high (0.2 – 2)
Heat stability	Excellent	Limited

Two-part silicone elastomers are provided as two-component (Part A and Part B or base and curing agent, the latter sometimes improperly named catalyst) to separate polymer, cross-linker and catalyst from each other. These two components are mixed in a fixed ratio prior to use to allow cross-linking only after mixing. Various additives may be included like fillers (e.g., a high surface area fumed silica with levels up to 25 % w/w), as these dramatically improve mechanical properties, or cure rate control agents to allow for enough time after mixing to handle the mixed material and to have enough “pot life” while casting the two-part material around the original.

The Art of Mold Making with Two-Part Silicone Elastomers

Mold making with silicone elastomers is an art. Many aspects are to be considered to preserve the original as well as to create the best possible copies. Originals need little preparation, but they must tolerate the process; staining or removing lustre on an old artefact would be catastrophic. Countermolds are made from various materials, from simple cardboard to fiberglass-reinforced polyesters.

Release agents are used to avoid adhesion from the two-part silicone elastomers onto the original and the countermold, or on any cured silicone surface when making a multipiece mold to avoid adhesion between mold pieces. Release agents are based on soaps in water, petrolatum in organic solvents, organic resins in water or fluoropolymers.

The silicone elastomer is cast after adequate mixing and de-airing under vacuum to eliminate bubbles. Operations range from one casting for a simple block mold to many castings for a multiple-piece mold, with a strong release agent applied on any cured silicone surfaces to avoid subsequent adhesion. “Pegs” may be created to ensure that all mold pieces will adjust to each other properly later, and to minimise defects from seal lines.

Various casting materials can be used to make copies, including plaster, peroxide-cured polyesters, or two-part organic resins like polyurethane or epoxy. Mold life is a critical aspect. Some casting resins can slowly swell the elastomer and cure within the silicone polymer network, actually forming an interpenetrating network (IPN). This can quickly lead to deformations in the copies with respect to the original or worse, adhesion of the copy to the mold. Among other casting materials are low melting point metallic alloys or waxes. Wax copies are used to make ceramic molds for high melting point metals.

Finishing the copy is most important. Thick layers of pigmented coatings are inadequate and would remove all the surface detail transferred from the original to the copy thanks to the silicone elastomers. Silicone elastomers are capable of transferring submicron surface details and render appearance as detailed as velvet or wood structure [88]. So the finishing step is where mold makers can express all their art. Pigments can be included in the casting resin to provide for an adequate starting color, or fillers can be added to adjust density and render feel when handling the object. Lustre on artefacts is developed by very thin coating layers brushed and padded away.

Application Fields

Much of the above is related to the use of two-part silicone elastomers for the reproduction of artefacts like museum pieces. The method has been used to reproduce very large objects like a horse with a man statue in France [89], a Chinese dinosaur skeleton [90] or a pair of Easter Island Moai statues [91], all full size! Yet such silicone elastomers are also used in our everyday life as dental impression materials (a challenging application, as molds are made on wet buccal surfaces and as moisture can interfere with the cross-linking reactions) or as intermediates to designing and preparing prototypes before market launch. More recently, bakery forms made from silicone elastomers were commercialised to cast and bake cakes.

11. Silicones in the Electronics Industries

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Before 1943, planes could maintain high altitudes for only a few minutes before ignition losses due to moisture condensing in the engines. A simple thickened PDMS grease (see Section 18) was the solution and an early example of the excellent dielectric properties of silicones. This application also illustrates key properties of silicones in the electronic industries like hydrophobicity and high dielectric breakdown (keeping moisture away and

avoiding loss of high voltage/low current signals), as well as their resistance to low or high temperatures, which allow use in harsh and critical environments [92].

Today, despite a higher cost to acquire, the number of applications involving silicones continues to increase, in some instances driven by Moore’s law (chip complexity doubling approximately every two years), but also by tighter specifications. The presence of more and smaller components (e.g., sometimes thousands in today’s cars) requires resistance to higher temperatures to ensure reliability and to avoid increasing the probability of failure.

Again, different silicones are used, and it is a combination of their properties that makes them perform well in various electronic and market applications (see Table 9).

Table 9. Markets for Silicones and their Key Properties in Electronic Applications

Silicone Product group	Electronics Major Markets <i>(V = markets where silicone products are used)</i>					
	Automotive	Consumer	Computer	Telecom- munication	Industrial	Medical
Lithography	V	V	V	V	V	V
Wafer Level Dielectric Layers	V	V	V	V	V	V
Wafer Level Passivation Layers	V	V	V	V	V	V
Die Encapsulants	V	V	V	V	V	V
Non-Conductive Die Adhesives	V	V	V	V	V	V
Conductive Die Adhesives	V	V	V	V	V	V
Lid Seal Adhesives	V	V	V	V	V	V
Electrically Conductive Materials	V	V	V	V	V	V
Gels	V			V	V	V
Conformal Coatings	V	V		V	V	V
Encapsulants	V			V	V	
Adhesives	V			V		
Sealants	V			V	V	
Foams				V		
Electromagnetic Shielding Materials	V			V		V
Primers	V	V	V	V	V	V
Cleaning Fluids	V	V	V	V	V	V
Thermally Conductive Gels	V				V	
Thermally Conductive Encapsulants	V				V	
Thermally Conductive Adhesives	V					
Thermally Conductive Phase Change Materials	V		V			
Thermally Conductive Fabricated Pads and Films	V	V	V	V	V	V
Thermally Conductive Greases / Compounds			V			

Silicone Product group	Physical Properties												
	<i>(■ = key property for the product in the application in which silicones and organics have similar properties; ▲ = key property for the product in the application in which silicones perform generally better than organics)</i>												
	Dielectric Constant	Dielectric Loss	High Electrical Resistance	Ion Purity	Dielectric Strength	Degradation Temperature (5)	Transition Temperature Tg and Tm (1)	Water Absorption	Flexibility	Surface Energy (2)	Optical Transparency and UV Stability	Environmental Friendliness and Inertness	Adhesion
Lithography	■	■	■	■			▲	▲	▲	▲ (4)	▲		
Wafer Level Dielectric Layers	■	■	■	■			▲	▲	▲	▲	▲		
Wafer Level Passivation Layers	■	■	■				▲	▲	▲	▲	▲		
Die Encapsulants	■	■	■	■		▲	▲	▲	▲		▲ (3)		
Non-Conductive Die Adhesives	■	■	■	■		▲	▲	▲	▲			■	▲
Conductive Die Adhesives						▲	▲	▲	▲			■	▲
Lid Seal Adhesives	■	■	■	■				▲	▲				▲
Electrically Conductive Materials						▲	▲		▲	▲		■	▲
Gels	■	■	■	■		▲	▲	▲	▲	▲	▲		
Conformal Coatings	■	■	■			■	▲	▲		▲	▲ (3)	▲	▲
Encapsulants	■	■	■	■	■	▲	▲	▲	▲	▲	▲ (3)		▲
Adhesives						▲	▲		▲				▲
Sealants						▲							▲
Foams	■	■				▲	▲		▲			▲	
Electromagnetic Shielding Materials						▲		▲					
Primers						▲				▲			▲
Cleaning Fluids				■				▲		▲		▲	
Thermally Conductive Gels			■			▲	▲	▲	▲	▲			
Thermally Conductive Encapsulants			■	■	■	▲	▲	▲	▲	▲			▲
Thermally Conductive Adhesives			■	■	■	▲		▲		▲			▲
Thermally Conductive Phase Change Materials			■	■	■			▲		▲			
Thermally Conductive Fabricated Pads and Films			■			▲		▲	▲			■	
Thermally Conductive Greases / Compounds			■	■	■	▲	▲	▲		▲			

- (1) Low Tg and Tm impacts the influence of temperature on key properties like dielectric properties
- (2) Surface energy impacts the wetting behaviour of the material
- (3) Relevant in optoelectronic applications
- (4) tunable wetting properties
- (5) Degradation temperature impacts Service temperature

The Relationship of Structural Properties in Electronic Applications

The Si-O-Si bond angle in a silicone polymer can vary between 105° and 180° [93], and the rotation is essentially free [94] around these bonds. As a result, the chains are very flexible and occupy a rather large volume, resulting in a high free volume in the material. Consequently, silicones exhibit a very low glass transition temperature ($T_g \approx -125^\circ\text{C}$). Low intermolecular interactions account for the low melting temperature ($T_m \approx -50^\circ\text{C}$) of silicone materials.

Once cross-linked, silicones are soft elastomers with hardness in the Shore A range if reinforced (see Section 14), or much softer in the absence of reinforcing filler and even gel-like if only partially cross-linked. In many applications, this “softness” allows relief of

stress induced by temperature changes as thermal dilatation mismatches. Silicone gels are compliant, self healing and outstanding for protecting thin wire-bonding from thermal shocks, vibration and corrosion. The response of their elastic and storage modulus is linear over a wide range of temperature and frequency.

Dynamic mechanical analysis has been carried out at various temperatures on a standard PDMS gel. The reduced shear storage and loss modulus and $\tan \delta$ are displayed against the reduced frequency for temperature ranging from -40°C to 100°C on Figure 18a and Figure 18b. The Arrhenius plot of the horizontal shift factor a_T can be seen on Figure 18c [95], showing a perfect fit with the Williams-Landel-Ferry (WLF) equation [96]. In that respect, silicone gels are exhibiting model behavior and could be used to study further fundamentals of cross-linked polymer mechanics. Other silicone materials also follow the WLF model as can be seen on the Arrhenius plot in Figure 18d, which compares the behavior of a silicone gel, a silicone elastomer and a silicone resin [95].

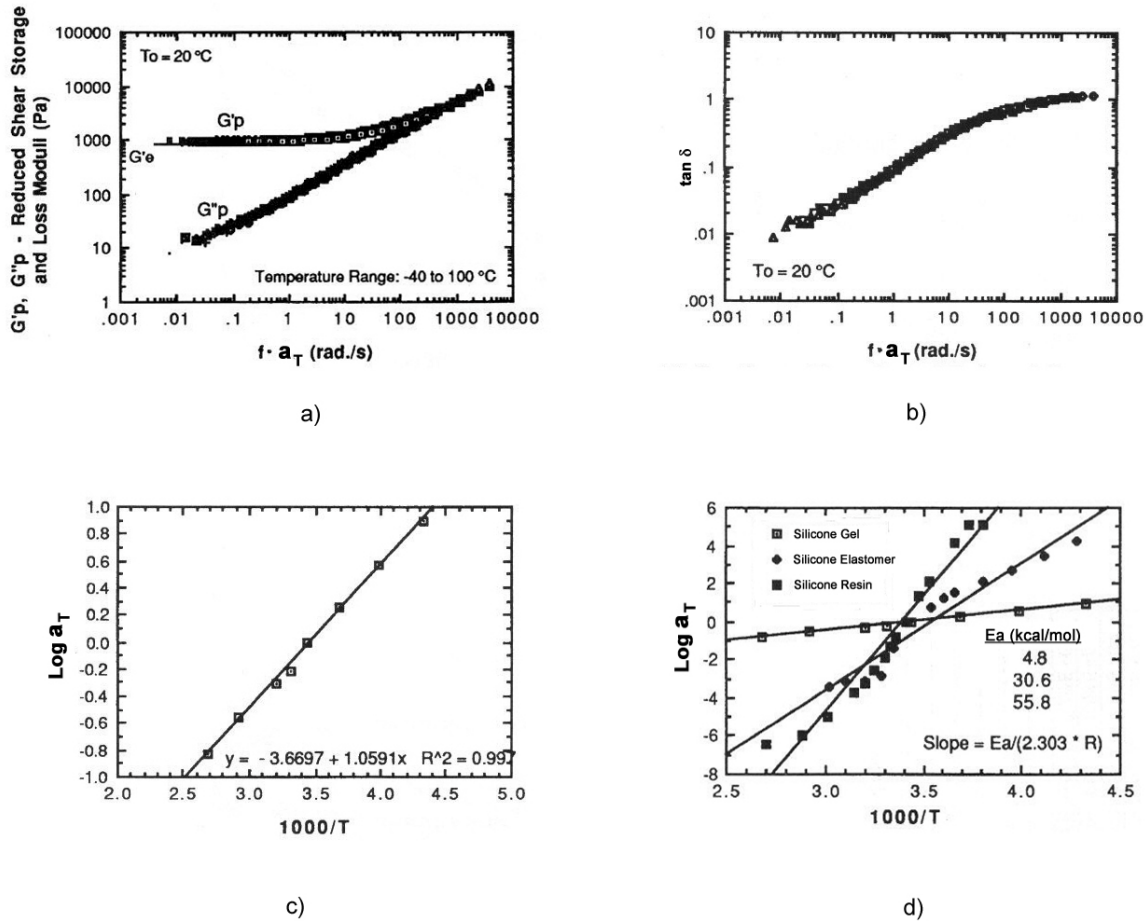


Figure 18. Dynamic mechanical analysis (DMA) shows: a) reduced shear storage and loss modulus of a standard silicone gel as a function of the reduced frequency at -40°C to 100°C ; b) $\tan \delta$ of the gel as a function of the reduced frequency temperature range from -40°C to 100°C ; c) Arrhenius plot of the horizontal shift factor for the gel; d) Arrhenius plot of the horizontal shift for a silicone gel, a silicone elastomer and a silicone resin.

The service temperatures of silicones can be extended by replacing some methyl groups by phenyl groups on the siloxane backbone. The random inclusion of different groups along the chain hinders natural ordering and crystallization. As a result, the T_m is either lowered or eliminated. The presence of phenyl groups also improves high temperature stability.

Electrical Properties of Silicones

Despite strongly polarized Si-O bonds, silicone polymers are nonpolar, as the Me side groups prevent Si-O dipoles from approaching each other too closely. As a result, the intermolecular forces are weak and mainly composed of London-van der Waals interactions that decrease with the square of the distance between molecules. Due to this ambivalent character of the PDMS polymer chain, the polarizability of the molecule accounts for a relatively high dielectric constant of silicones in comparison to a nonpolar polymer like polyethylene (see Table 10). As expected, silicone copolymers in which Me groups have been substituted with more polarizable groups are not better either.

Table 10. Dielectric Properties of Various Polymers [97]

Polymer	Dielectric constant at 100 Hz	Dissipation factor at 100 Hz	Dielectric strength at 60 Hz	Volume resistivity <i>ohm.cm</i>	Tg <i>K</i>
High density polyethylene	2.30	0.00011	811	$2.2 \cdot 10^{16}$	148
Cis-polyisoprene	2.26	0.0094	577	$7.1 \cdot 10^{16}$	210
Poly methylmethacrylate	3.03	0.057	608	$1.2 \cdot 10^{16}$	382
Poly dimethyl siloxane (Me ₂ SiO) _n	2.86	0.00025	552	$5.3 \cdot 10^{14}$	150
Poly diphenyl dimethyl siloxane (φ ₂ SiO) _{5.5} (Me ₂ SiO) _{94.6}	2.90	0.00041	661	$9.8 \cdot 10^{14}$	151
Poly phenylmethyl dimethyl siloxane (φMeSiO) _{7.5} (Me ₂ SiO) _{92.5}	2.87	0.00010	661	$3.0 \cdot 10^{14}$	149
Poly phenyl methyl dimethyl siloxane (φMeSiO) ₃₀ (Me ₂ SiO) ₇₀	2.99	0.00024	720	$4.4 \cdot 10^{14}$	176
Poly trifluoropropyl methyl siloxane [(CF ₃ CH ₂ CH ₂)MeSiO] _n	6.85	0.109	342	$2.7 \cdot 10^{11}$	199
Viton [®] fluoroelastomer	8.55	0.0403	351	$4.1 \cdot 10^{11}$	255

The dielectric constant of PDMS increases with the degree of polymerization (DP) of the siloxane backbone before quickly reaching a plateau value (see Figure 19) [98]. This effect is related to the siloxane-to-methyl-groups ratio, which quickly increases, particularly in the shortest DP polymer. At higher DP, adding one more unit has little impact on the permittivity of the media, which explains the plateau region.

In most organic polymers, the strong attractions between polymer chains diminish as the temperature increases, so many dependent properties change significantly. For silicones, the intermolecular forces are low and do not change much with temperature. Consequently, viscosity, mechanical properties, dielectric properties and many physical properties are little affected over a wide range of temperatures. Electrical properties like

dielectric constant and the dissipation factor are also little affected over a wide range of frequencies [99-100-101].

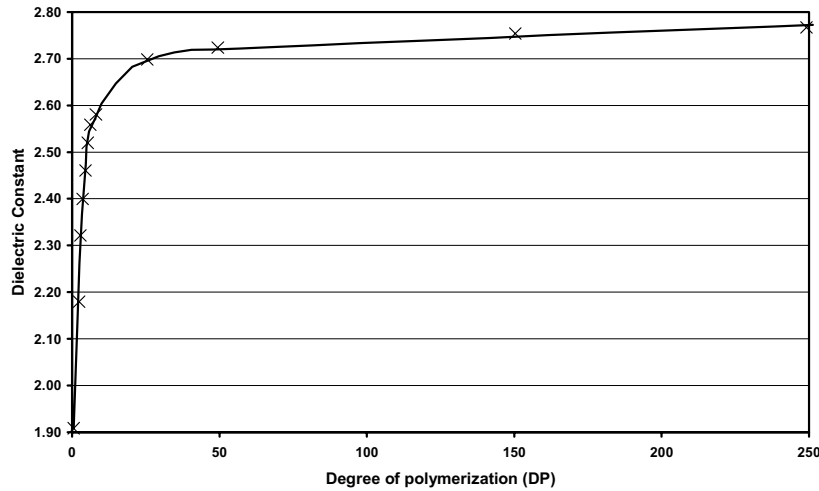


Figure 19. Influence of degree of polymerization on the dielectric constant of polydimethylsiloxanes, measured at 1000 Hz at 23 °C.

The volume resistivity of silicones is marginally lower than organic materials; ion concentration tends to be low in PDMS and dependent only on the presence of impurities like residual traces of polymerization catalysts or other impurities due to presence of reinforcing fillers. However, ion mobility is favored because of the high free volume in PDMS [97].

Although not entirely related to volume resistivity, dielectric strength is also influenced by the presence of material impurities [97-98-99-100-101-102]. For a given matrix, the path for dielectric breakdown follows the weakest path as far as resistivity is concerned. Here again, the high free volume of silicone-based materials lowers their dielectric strength in comparison to organic materials.

The dielectric properties of silicones are good, but not exceptional in comparison with organics. The success of silicone-based products is certainly related more to their stability over a wide range of temperature, humidity and frequency.

Water Absorption

Although often overlooked, water absorption is a key property for products used in electronics, as absorbed water reduces dielectric properties and can contribute to corrosion. Yet, in many electronics applications where silicones are used, it is too simplistic to think that because of their hydrophobicity and water repellency, silicones provide better device protection against corrosion than organics.

Corrosion occurs if reactants like oxygen, water and ions are simultaneously present at the interface. Silicone materials are very permeable to gases and therefore cannot limit

oxygen or water vapor from reaching a metal interface. However, ions surrounded by several layers of water molecules are poorly soluble in PDMS and, being large clusters, they have a very low coefficient of diffusion in any polymer matrix. Absorbed water molecules in the protective layer are like stones across the river for ions: they use these favorable “water” paths to migrate across the layer at a much greater rate of diffusion [103]. Because of their high permeability, silicones will uptake water quickly compared to epoxies. Yet at saturation level, water content in silicones is ten times lower than in epoxies (see Figure 20) [104]. This is the main reason why silicones are so effective when used as corrosion protective materials. An additional benefit in electronics is that when temperature increases suddenly, water diffuses easily from silicones compared to organics and without local pressure build-up (“popcorning” issue).

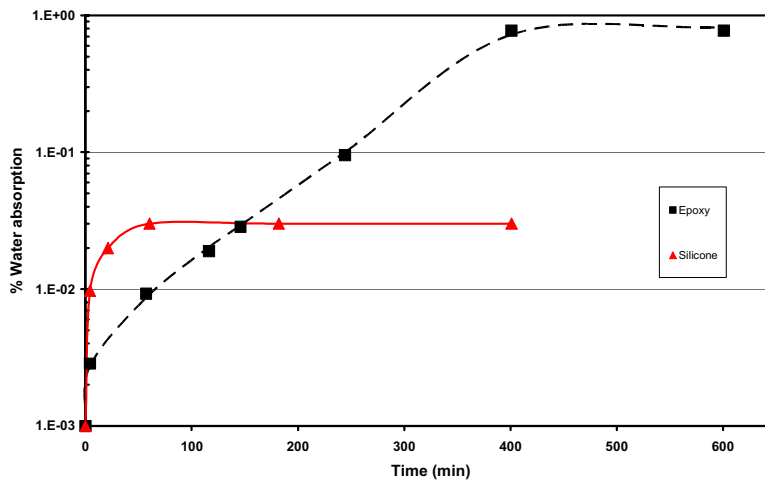


Figure 20. *Water absorption of PDMS vs. epoxy in electronic products.*

Thermal Conductivity

With trends toward miniaturization and higher power electronics, heat dissipation and protection at component interfaces is becoming more critical. Silicone thermal conductivity is rather low if compared to metals (see Table 11). However, it is about ten times better than air, which is most often responsible for poor heat conduction at metal-metal or metal-plastic interfaces.

Table 11. **Thermal Conductivities of Various Materials**

Material	Thermal conductivity (<i>W / m.K</i>)
Silver	417.3
Copper	393.7
Silicone, thermally conductive (PDMS + silver filler)	0.7 - 8.0
Silicone (PDMS)	0.2
Epoxy	0.2
Air	0.03

Because of low surface tension [4], PDMS has an enormous advantage that is not demonstrated by its intrinsic heat conductivity if compared to organics. PDMS allows good surface wetting, and so displaces air at interfaces, reducing heat resistance between components. This in particular has driven the penetration of silicones in electronics thermal management applications.

12. Silicones for Photonics

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As the photonics market develops, there is a continuing need to bring costs down. For opto-electronics, polymer-based components and structures are being considered because they are inherently easier to process than glass-based materials. Polymers can be batch processed by spin coating or stamping, but also processed continuously via printing or extrusion. In addition, this processing can take place at ambient temperatures and pressures. A variety of polymer systems have been investigated in photonics with varying degrees of success.

Light transmission through polymers can be limited by electronic transitions in the UV-visible region or by vibrational absorptions in the near-IR or IR, including overtones. These sources of loss are specific to each polymer. Intrinsic light losses tend to be higher with polymers than with glass-based materials. Under high flux, polymer degradation can occur: organics will yellow because of the heat generated, and they can also degrade because of photo-initiated oxidation. Despite these shortcomings, polymers are considered to take advantages of their inherent benefits. These benefits include ease of processing (resulting in lower-cost production) and also some material-specific functionality like high thermo-optic coefficient (see discussion below). Optical applications are considered, despite the higher intrinsic light loss generally associated with polymers, because the loss is not as critical for short-length (e.g., less than one meter) applications such as passive waveguides for communications between circuit boards, between integrated chips or even for lenses for light emitting diodes (LED).

In addition to their excellent thermal stability, mechanical properties and ease of processing, silicones are highly transparent to radiation in the visible all the way down to UV. Silicones also have good transmission at selected near-IR wavelengths [105]. Very low levels of Rayleigh scattering can be achieved with silicones. Therefore, silicone-based polymers possess a set of properties making them suitable for waveguide applications, as well as for lenses and encapsulants through which light must travel.

Necessary Properties for Photonics Applications

For waveguide applications, critical material attributes are [106]:

- Low dielectric constant, and this usually also implies low refractive index
- Transparency with negligible light loss due to UV-visible electronic or IR vibration absorptions

- Homogeneity to minimize scattering
- Low intrinsic birefringence, and in most applications, low stress-induced birefringence
- Satisfactory thermophysical properties for the desired application

The most common silicone polymers are linear PDMS based on $\text{Me}_2\text{SiO}_{2/2}$ or D units with refractive indices approximately 1.40 - 1.42. More complex as well as more rigid structures can be engineered by including T or Q units (see Section 1). Some methyl groups along the chain can be substituted with phenyl groups to increase the refractive index to approx. 1.55 or with trifluoropropyl groups to reduce the refractive index below 1.40.

In the following section, important characteristics including dielectric properties, thermophysical properties and absorption characteristics will be developed and highlighted with examples.

Dielectric Properties. A low dielectric constant is desired because it minimizes light absorption by the material. The absorption and complex dielectric constants are linked through the Kramers-Kronig relations. Silicones in general have low dielectric constants when compared to other optically transparent plastics. The dielectric constant depends on the overall modulus of the system, state of cure, and overall system composition (i.e., type of polymers, cross-linkers and additives used). For PDMS with viscosities between 10 to 60,000 cSt, the dielectric constant ranges from 2.72 to 2.75 when measured from 100 to 10,000 Hz at 25 °C [107]. The dielectric constant for PDMS also varies with temperature: at 800 Hz, it measures 2.8 and 2.3 for 20 °C and 200 °C respectively [108]. For a polymethylphenyl siloxane, the dielectric constant has been measured at 2.98 at 25 °C and independent of frequency from 100 to 1,000,000 Hz [109]. By comparison, polymethylmethacrylate (PMMA) has dielectric properties that range from 3.6 at 50 Hz, 3.0 at 1000 Hz, and 2.6 at 1,000,000 Hz when measured at 25 °C [110], and polycarbonate (PC) has a dielectric constant of 3.02 at 1000 Hz [111]. Because of the lower dielectric sensitivity to frequency, siloxane polymers in general have lower levels of dispersion than common organic polymers.

Thermophysical Properties. Siloxane polymers are not prone to yellowing, and if care is taken to remove catalyst impurities, they have very good thermal stability (see Section 1). The inclusion of phenyl groups leads to polymers that are stable for short durations at 300°C under nitrogen or air (see Figure 21) [112]. Many siloxanes have continuous temperatures specified at 150 °C or above. For comparison, the continuous use temperature for PMMA is < 90 °C and for PC is 121 °C [111].

Waveguides made from silicones maintain their shape without cold flow because the materials are cross-linked. Because the T_g of PDMS is very low, stress birefringence remains low at most temperatures. The stress-optical coefficient for PDMS is $1.35 \times 10^{-10} \text{ m}^2/\text{N}$ at 20 °C and 632.8 nm [113]. For polymethylphenyl siloxane, the coefficient is reported to be slightly higher at $5.73 \times 10^{-9} \text{ m}^2/\text{N}$ [114].

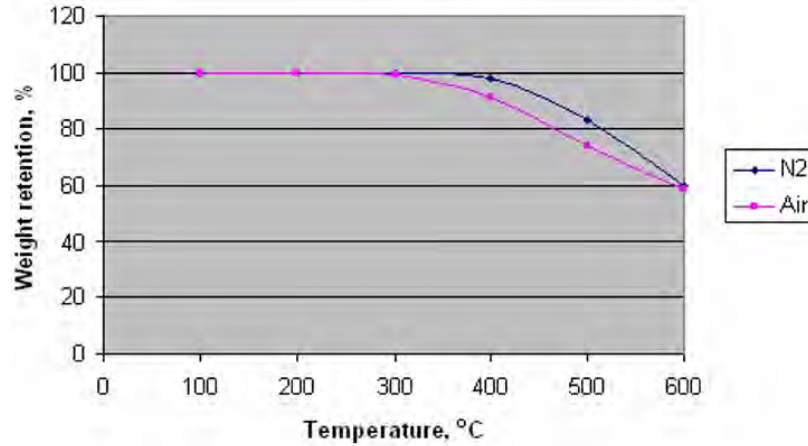


Figure 21. Thermal gravimetric analysis of a poly methylphenyl dimethyl siloxane copolymer under nitrogen or air under a temperature ramp rate for the testing of 10 °C/min.

The thermo-optic coefficient (change of the refractive index vs. temperature), dn/dT , for siloxanes varies from -1.5×10^{-4} to -5×10^{-4} , depending on composition and cross-linking density [106]. The capability to tune dn/dT can be of use in some applications like thermally controlled variable optical attenuators and athermalizing planar light circuit components. For PMMA, $dn/dT = -1.1 \times 10^{-4}$ below T_g , which is approximately 105 °C [115].

Phonon and Absorption Characteristics. Methyl siloxanes do not show characteristic absorption bands in the UV or visible spectrum, while methylphenyl copolymers have characteristic absorptions at 270, 264 and 250 nm. Both have many absorption bands in the NIR region (see Table 12) [105].

Table 12. Light Loss Characteristics of Silicone Polymers or Copolymers at Various Wavelengths

<i>Silicone Polymer or copolymer</i>	<i>Loss at specific wavelength dB/cm</i>					
	<i>1550 nm</i>	<i>1310 nm</i>	<i>850 nm</i>	<i>633 nm</i>	<i>400 nm</i>	<i>300 nm</i>
Dimethyl	0.67	0.14	< 0.01	< 0.01	0.03	0.09
Dimethyl methylphenyl	0.66	0.28	0.03	0.03	0.04	0.24
Methylphenyl	0.62	0.35	< 0.01	< 0.01	< 0.01	0.55
Trifluoropropyl methyl - 1	0.54	0.16	< 0.01	< 0.01	< 0.01	< 0.01
Trifluoropropyl methyl - 2	0.35	0.07	0.12	0.22	0.64	1.36
Phenyl resin - 1	0.49	0.41	0.01	0.02	0.06	2.39
Phenyl resin - 2	0.39		0.03	0.05	0.11	2.94

Phenyl groups or trifluoropropyl groups can be added to reduce the absorptions in the 1500-1560 nm wavelength regions. However, the phenyl can have a negative impact on the absorptions at 1100, 1280-1320 nm. Despite these trade-offs, silicones are capable of excellent loss properties in the datacom wavelengths and certainly are adequate for short-range applications in the wavelength bands of interest for telecom (see Figure 22).

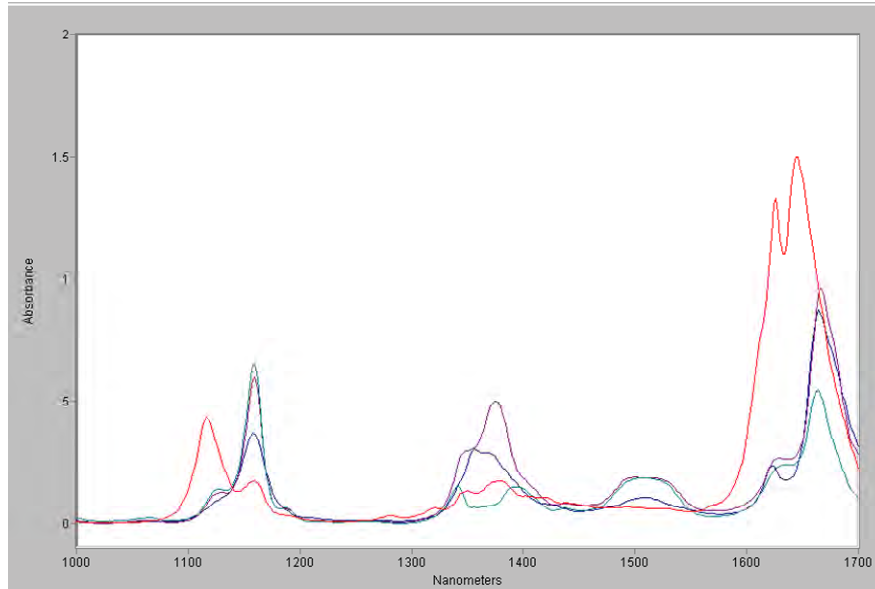


Figure 22. NIR absorption spectra of a PDMS polymer (in teal) and shifts in absorption when different substituents are added. In general, decreased absorbance at 1160 nm and 1500 nm and increasing absorbance at ~ 1630 nm results from increasing the phenyl content of the system (in red-resin and in purple-polymer). The addition of trifluoropropyl groups reduces absorption around 1160 and 1500 nm (in blue).

In summary, silicones possess an interesting set of properties for photonic applications when compared to organic polymers. Silicones display high-temperature stability, which makes them compatible with solder reflow processing or in “under-the-hood” high-temperature applications, and they can be processed at room temperature. Silicones also have the optical characteristics necessary to enable them to function in waveguides with acceptable losses at telecom wavelengths and with very low losses over data-communications wavelengths.

13. Silicone in Medium to High Voltage Electrical Applications

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The use of silicones in these applications is much related to cable end terminations or silicone rubber connections made at the end of underground high voltage cables insulated with polyethylene, as well as to silicone insulators for power lines.

Key benefits from silicones are their high electrical resistivity, resistance to environmental degradations and to electrical aging as well as their hydrophobicity, which results in lower assembly and maintenance costs [116-117].

Silicone Cable End Terminations

Modern materials allow pre-assembly and thus avoid problems associated with the use of molten casting material or mistakes made during manual assembly on the construction

site. Today cable accessories are completely built at the supplier. Typically they consist of rubber terminations made of different insulating silicone rubbers.

Silicones allows for two types of design:

- Push-on technique where a PE ring acts as a space holder until placement, and using silicone rubbers with hardness from 35 to 50 Shore A
- Cold shrink technique using softer silicone rubbers with hardness from 25 to 35 Shore A

Insulation is made without chemical bonding between the termination and the cable, and it relies on the elastomeric characteristics of the silicone termination to exclude any entrapped air, particularly in areas of high electrical field and around the edges at the cable end. The high gas permeability of silicones allows any included air to diffuse out to leave an air-free joint.

Such silicone rubber cable end terminations are produced by rubber injection molding using a silicone high consistency rubber (HCR) or by liquid injection molding using a two-part liquid silicone rubber (LSR).

Silicones provide overall electrical insulation because of their high dielectric strength (see Section 11). In addition to their good resistance to high temperature, UV and ozone, they are hydrophobic and so do not promote surface insulation failures. But more important, specially formulated silicones have been developed to smooth the electrical fields within the connection end and to ensure long-term performance. This is achieved in composite cable terminations either using some electrically-conductive silicone rubbers or, in more modern and smaller accessories, shaped deflectors made from silicone rubbers with medium electrical permittivity (see Figure 23).

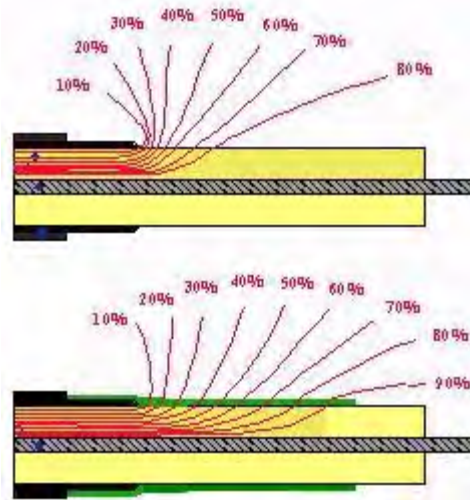


Figure 23. *Field line density in a cable end termination at the cut of the screen without control (upper figure) or with a nonconductive/high permittivity field control silicone rubber (in green; lower figure).*

Silicones are appreciated in cable end terminations because of their resistance to erosion caused by radiation. As silicones do not absorb UV-visible sunlight, they are not prone to chalking or cracking. Such phenomena are typical with organic-based materials and, associated with dirt pickup and humidity, can lead to a significant reduction of insulation properties.

Silicone resistance to so-called “tracking” is also higher than with organic-based insulation materials. Tracking is the formation of electrically-conductive surface paths under intensive electrical surface leaks and discharges. In organic materials, this leads to the formation of carbon-based decomposition products that unfortunately show high conductivity. With silicones, even if poorly designed or not properly assembled, decomposition leads to nonconductive silica, and silicones will meet the highest class of electrical erosion resistance.

Silicone Insulators

Another key property is hydrophobicity, particularly for electrical insulators, or devices installed between power lines and supporting structures. Water on an insulator made of a silicone elastomer remains as droplets and does not form a continuous film because of the low surface energy of the silicone elastomer surface [118-119-120]. This reduces surface currents on the insulator. Surface hydrophobicity is maintained even after surface discharges or deposition of airborne pollution because of the presence of low molecular weight, unreacted polydimethylsiloxane species in the composition of the silicone elastomers. These species can migrate to the external surface and maintain low surface energy or hydrophobicity [121]. Insulators made of silicone elastomer therefore need little cleaning or maintenance and perform over a long period of time (see Figure 24).



Figure 24. *Comparison of an insulator after 23 years of use and exposure to pollution (left) vs. a retained sample kept at RT (right). Both still show excellent hydrophobicity as indicated by the high contact angle of the water droplets. (Picture courtesy of Lapp Insulators GmbH & Co.KG).*

14. Silicones in Transportation: Automotive and Aviation

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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 13) [122].

Table 13. Typical Mechanical Properties of Selected Rubber Families

<i>Material</i>	<i>Unit</i>	<i>Silicone</i>	<i>Natural Rubber</i>	<i>EPDM</i>	<i>Neoprene</i>
Tensile strength	<i>MPa</i>	4 - 12	28	24	28
	<i>psi</i>	990 - 1265	4000	3500	4000
Elongation at break	%	570 - 1000	700	550	500
Hardness range	<i>Shore A</i>	20-90	30-90	25-85	35-90
Min. operating temperature	$^{\circ}\text{C}$	- 60 (*)	- 60	- 50	- 40
Max. operating temperature (continuous)	$^{\circ}\text{C}$	230	100	140	100
Relative density		1.15	0.92	0.86	1.23

(*) Special grades down to -116 $^{\circ}\text{C}$

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 (see Section 1).

Silicone rubber compounds are typically delivered as one-part materials to be cross-linked 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 [123].

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 -CH₂-CH₂-CF₃ groups) offer a step change in fluid resistance (see Table 14) [122]. 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 14. Fluid Resistance of Standard and Fluorosilicone Rubbers

<i>Rubber Type</i>	<i>Water</i> <i>3 days / 100 °C</i>		<i>ASTM Oil #3</i> <i>3 days / 150 °C</i>		<i>Toluene</i> <i>7 days / 24 °C</i>	
	Delta duro	% swell	Delta duro	% swell	Delta duro	% swell
MQ	- 5	+ 5	- 25	+ 35	na (*)	na (*)
VMQ	- 5	0	- 20	+ 35	na (*)	+ 205
FVMQ	0	0	- 5	+ 5	-10	+ 20

(*) 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.

15. Silicones in the Plastics Industry

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Silicones are used in the plastics industry as additives for improving the processing and surface properties of plastics, as well as the rubber phase in a novel family of thermoplastic vulcanizate (TPV) materials. As additives, silicones, and in particular polydimethylsiloxane (PDMS), are used to improve mold filling, surface appearance, mold release, surface lubricity and wear resistance. As the rubber portion of a TPV, the cross-linked silicone rubber imparts novel properties, such as lower hardness, reduced coefficient of friction and improved low and high temperature properties.

Low molecular weight PDMS polymers, with viscosities less than 1000 cSt, are used extensively by the plastics industry as external release agents applied on the mold surface prior to injection molding. To eliminate an external application during processing, higher molecular weight PDMS materials, with viscosities ranging from 10,000 cSt to 60,000 cSt, have been used as internal additives in thermoplastic polymers to give processing advantages and surface property improvements [124-125]. Due to the incompatibility between dimethyl siloxanes and most thermoplastics, the PDMS is driven to the surface. For example, the solubility parameter for dimethyl siloxane is $14.9 \text{ MPa}^{1/2}$ and the solubility parameter for nylon 6 is $27.8 \text{ MPa}^{1/2}$ [126]. A concentration of the PDMS at the surface results in the observed processing and surface property benefits.

A more recent advancement in the field of PDMS additives is the use of ultra high molecular weight (UHMW) PDMS, with viscosities ranging from 10 to 50×10^6 cSt [127]. Additives are now available with 50 weight percent UHMW PDMS in various thermoplastic carriers and as pellets so as to allow easy addition of the additive directly to the thermoplastic during processing. An important improvement obtained using UHMW PDMS is that the loading of PDMS in the concentrated additive is increased from approximately 20 to 50 weight percent. As seen in Figure 25, the UHMW PDMS forms stable droplet domains in the thermoplastic carrier, with an average particle size of 2 microns.

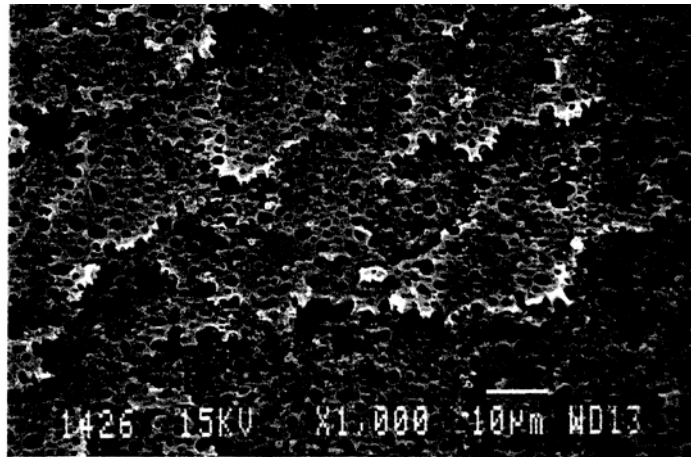


Figure 25. *Photomicrograph of a 50% UHMW PDMS dispersed in polypropylene and showing the fine dispersion of the silicone into the organic phase.*

UHMW PDMS results in the same processing benefits such as improved mold release, easier mold filling, and lower extruder torque as compared to lower molecular weight PDMS, but it eliminates the “bleed-out” that can occur after processing. This benefit is clearly seen when comparing the print adhesion to polypropylene films containing various additives (see Figure 26). Low molecular weight PDMS (30,000 cSt) and common organic mold release additives significantly reduce the print adhesion due to their migration to the surface and eventual blooming or bleed-out from the plastic part. Conversely, the UHMW PDMS does not reduce the print adhesion because its high molecular weight reduces its mobility and effectively anchors the additive into the plastic.

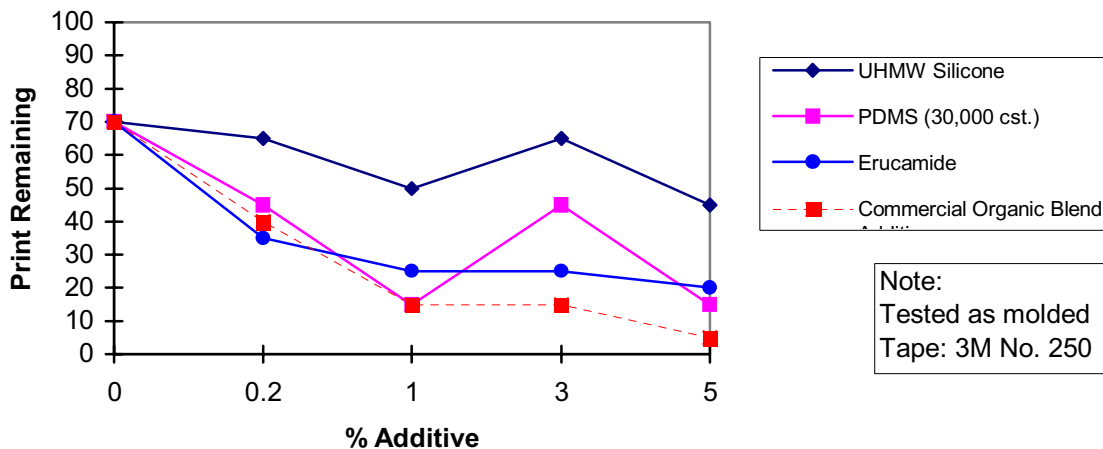


Figure 26. *Print adhesion to polypropylene films containing various additives and tested with 3M tape no. 250 per ASTM D3359.*

UHMW PDMS additives are often used to improve the wear or abrasion resistance or to reduce noises generated by the motion of plastic parts. These benefits are reflected by the decrease in the coefficient of friction (see Figure 27). A rotating cylinder method was used to generate the coefficient of friction results, with a constant force of 2 kg and a

varying velocity until sufficient heat generation occurred and the cylinder and barrel fused. The addition of 3 weight percent UHMW PDMS significantly reduced the coefficient of friction as well as delayed the fusing until much a higher velocity.

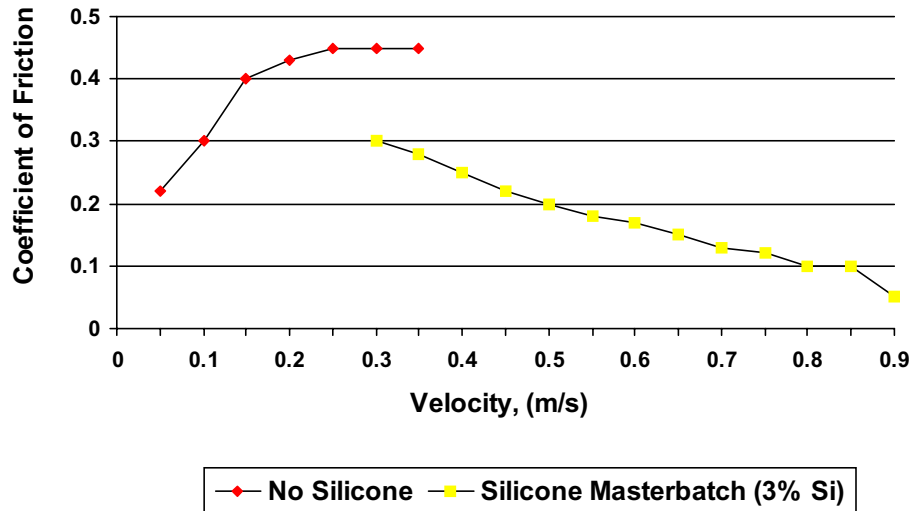


Figure 27. Coefficient of friction measurements from pressure-velocity plots for polypropylene without or with UHMW PDMS additive.

Recently, a novel family of TPV products has been introduced and is based on cross-linked silicone rubber dispersed into various engineering thermoplastics [128]. The dispersion of the silicone internal phase is produced by dynamic “vulcanisation” or cross-linking of silicone polymers within the thermoplastic organic phase and results in a stable droplet type morphology (see Figure 28).

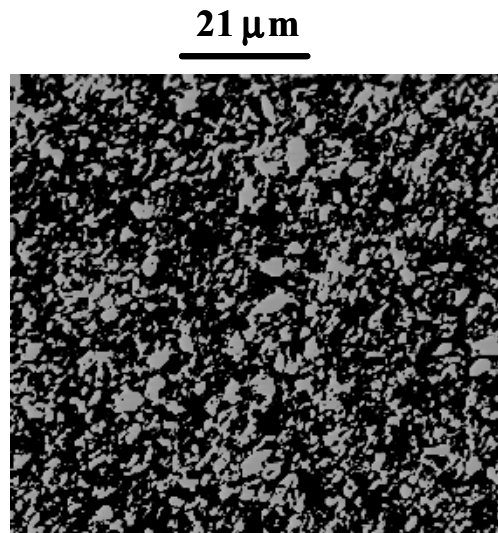


Figure 28. Transmission electron micrograph depicting the morphology of a silicone-based TPV (light gray areas are silicone rubber particles dispersed within the organic continuous phase).

Such a stable morphology is achieved only by using appropriate compatibilizers to ensure compatibility between the silicone and organic thermoplastic phases, which have very dissimilar solubility parameters. As for other TPVs, such thermoplastic compounds are melt processable and fully recyclable.

Silicone TPVs have been commercialized using various engineering thermoplastics, but of greatest interest are polyamide and polyurethanes thermoplastics. Silicone polyamide TPV has found use as the jacketing material in automotive brake cables due to its excellent temperature and chemical resistance [128]. Silicone polyurethane TPV combines the benefits of excellent abrasion resistance from the polyurethanes as well as the lower coefficient of friction and improved temperature properties from the silicone rubber. The properties of silicone polyurethane TPV vs. a well known EPDM-PP TPV are compared in Table 15. In particular, the silicone polyurethane TPV outperforms the EPDM-PP TPV in oil resistance due to the miscibility of oils in polypropylene.

Table 15. Comparison Between a Silicone Polyurethane TPV vs. a EPDM-PP TPV: Initial Properties and After Aging in Air or Oil at Elevated Temperatures

<i>Property</i>	<i>Testing Method</i>	<i>Silicone polyurethane TPV</i>	<i>EPDM-PP TPV</i>
Initial:			
Hardness, <i>Shore A</i>	ASTM D2240	71	66
Tensile strength, <i>MPa</i>	ASTM D412, Die D	16	6.5
Elongation at Break, %	ASTM D412, Die D	600	457
70 hours in air at 175°C:			
Change in hardness, <i>Shore A</i>	ASTM D573-99 for heat aging.	+7	-5
Change in tensile strength, % (*)	Same methods as above for testing	+6.3	-32
Change in elongation at break, % (*)		+12	-20
70 hours in IRM 903 oil at 100°C:			
Change in hardness, <i>Shore A</i>	ASTM D471-98 for fluid immersion.	-9	-19
Change in tensile strength, % (*)		-23	-29
Change in elongation at break, % (*)	Same methods as above for testing	-2.5	-40
Volume swell, %		+23	+80

(*) change expressed as percentage of initial value.

Compared to thermoset silicone rubber, a silicone TPV offers the added benefit of bondability to various thermoplastics without the use of primers or adhesives via coextrusion and comolding/overmolding. Silicone polyurethane TPV was overmolded onto “cold” (i.e., room temperature) inserts of various thermoplastics and the bond strength was testing according to ASTM D1876. An example of the peel force is shown in Figure 29.

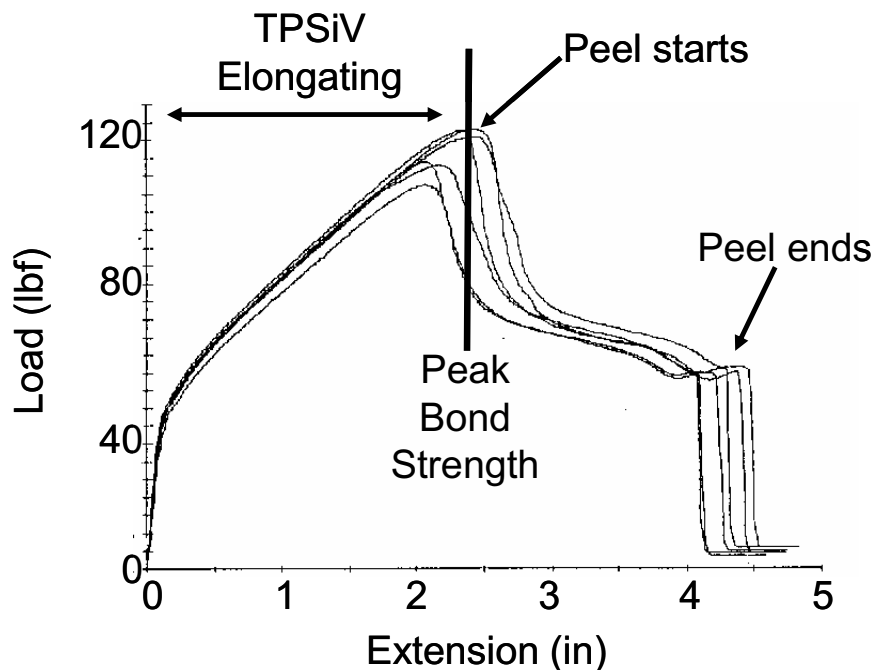


Figure 29. Peel force of a silicone polyurethane TPV molded on polycarbonate substrate (Multiple curves representing 6 repeats).

The soft TPV first elongates until the bond begins to peel at the peak force. A bond strength of approximately 20 N/mm was observed on PC and ABS, while a bond strength of approximately 8 N/mm was observed on nylon. The bonding failure on PC/ABS is cohesive, while the bond failure on nylon is adhesive. This excellent bond strength has resulted in silicone TPV being an ideal material for applications that require the combination of soft and rigid plastics, such as overmolded electronic equipment (soft-touch grips and buttons) and overmolded seals.

The applications of silicones in the plastics industry continue to grow as more benefits are identified by combining the unique properties of thermoplastics and silicone.

16. Silicones in Personal Care Applications

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Silicones used in personal care applications are of diversified types, including cyclic, linear, or organo-functional polydimethylsiloxanes (PDMS), as well as silicone elastomer dispersions and resins. This wide range of molecules provides benefits that impact the performance of almost every type of beauty product, conferring attributes such as good spreading, film forming, wash-off resistance, skin feel, volatility and permeability.

The first use of silicone in personal care applications dates back to the 1950s, when a PDMS was incorporated into a commercial formulation to provide skin protection [129].

Since then, the use of silicones has kept increasing, along with the evolution of the knowledge around those materials (see Figure 30). Further to their first success, silicones made another breakthrough in the antiperspirant segment during the 1970s. Low molecular weight cyclosiloxanes were used as volatile carriers for the antiperspirant active, enhancing consumer acceptance of products thanks to the pleasant skin feel they could confer as well as their nonstaining properties [130].

Silicones then made their entry into hair care products. Amino-functional polymers were incorporated into styling mousses and rinse-off conditioners, while fluid or emulsion forms of high molecular weight PDMS were formulated into two-in-one conditioning shampoos. More recently, silicone elastomer dispersions were introduced to the market and gave formulators access to a new sensory dimension in terms of silkiness. Today, silicones find a use in virtually all types of personal care products, in segments as diversified as hair care, hygiene, skin care, sun protection or color cosmetics.

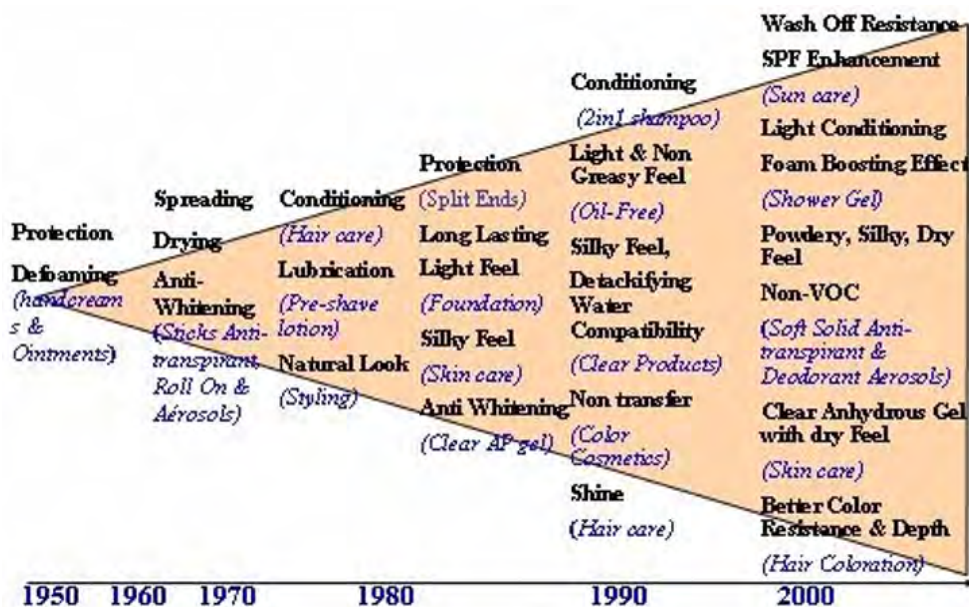


Figure 30. History of silicone uses in personal care.

Types of Silicones Used in Personal Care Applications

The versatility of silicones accounts for their wide use in beauty care products. This diversity stems from the unique set of physicochemical properties of PDMS as well as the variety of polymer types that can be used. Silicones incorporated into personal care products vary in molecular weight, structure or substituents attached to silicon atoms.

The most commonly used silicones are linear PDMS of various viscosities, ranging from the shortest possible chain, hexamethyldisiloxane with a viscosity of 0.65 cSt, to polymers with high degrees of polymerization and viscosities over 10^6 cSt, often called silicone gums. Cyclic PDMS with 4, 5 or 6 dimethylsiloxane units is also widely

encountered in formulations. Because of their volatility, low molecular weight linear and cyclic PDMS materials are often referred to as volatile silicones.

Changing the structure and going from linear species to network or cross-linked systems leads to silicone resins and silicone elastomer dispersions. Such resins contain a number of T or Q units in a three-dimensional structure resulting from the hydrolysis/condensation of the corresponding initial silane monomers. The preparation of those materials is described in Section 1. Silicone elastomer dispersions are cross-linked gels that can be prepared through a hydrosilylation reaction. The reaction involves low levels of catalyst, usually platinum derivatives, and is generally run into an adequate solvent. SiH-containing silicone polymers are reacted with di-vinyl materials to link independent silicone chains. If the reaction is carried out in cyclic PDMS as the solvent, it leads to the formation a swollen and loosely-reticulated network or a silicone elastomer dispersion.

Substitution of methyl with other groups allows significant modification of PDMS properties, accessing other benefits. Most common are linear alkyl, phenyl, polyether or aminoalkyl groups. This leads respectively to silicone waxes (if alkyl groups of sufficient length are grafted onto the backbone), water dispersible polymers or substantive polymers.

All these materials can be prepared by hydrosilylation, through the addition of various molecules bearing a vinyl group on a SiH-containing silicone polymer. Another route to such polymers involves the manufacturing of specific chlorosilanes to generate functional polymers after hydrolysis.

Silicone Benefits in Beauty Care Products

In skin care, a fundamental aspect is the “feel” provided, or how the product is perceived on skin upon and after application. Silicones convey a very differentiated feel to cosmetics, described as smooth, velvety, nongreasy and nontacky [131]. They can also help diminish the tackiness induced by other raw materials present in the formulation. They are appreciated by formulators because of their film-forming properties, providing substantivity, wash-off resistance and protection. PDMS materials have been found to be noncomedogenic and nonacnegenic, meaning they are not expected to encourage undesired skin pore clogging or acne [132]. Their antifoam characteristics also help reducing the so-called “soaping effect,” an undesired foaming phenomenon observed in skin creams formulated with soap-based emulsifiers (see Section 3).

Sun care products are devoted to protecting and reducing damage to skin induced by UV radiation. Here, the formulator’s goal is to create on skin a film of UV-protective actives as homogeneous and as resistant to water removal as possible, even after a swim. Low molecular weight silicones like cyclics are included in sun care formulas to improve spreading [131-132-133]. Because of their hydrophobicity, PDMS and in particular high molecular weight polymers, have demonstrated substantivity. In such formulations, the active can be made more resistant to wash-off. This helps maintain the level of sun

protection of the formulated product after application on skin. In addition to wash-off resistance, alkylmethylsiloxanes have also been shown to enhance the sun protection factor (SPF) of products containing either organic or inorganic sunscreens.

In color cosmetics, silicones are used to confer either a matte or a shine effect [134]. Phenyl silicones, because of their higher refractive index, help produce glossy films. This accounts for their use in products such as lipsticks or lip glosses, where shine is sought after. On the contrary, if a matte effect is desired, as in foundation applications, silicone elastomer dispersions can be used, possibly because of their effect on light scattering. Alkylmethylsiloxanes are also appreciated because of their ability to provide, together with a pleasant feel, a waxy consistency and an increased compatibility with organic ingredients commonly used in such formulations [135]. Low molecular weight silicones are used in facial cleansers because of their low surface tension, good wetting properties and ability to remove dirt or color cosmetic residues, while delivering a dry and nongreasy feel [136].

Hair conditioning relates to softness, volume, body, sheen, feel and fly-away control [135]. This also includes hair protection from daily aggressions such as chemical treatments, combing or drying. Silicones are most often used in hair care because they can provide these conditioning benefits, consequently becoming key ingredients in shampoo or after-shampoo products. High molecular weight PDMS as well as aminoalkyl copolymers (also called amodimethicones) can deposit on hair and are particularly efficient in making hair easier to comb [129]. In the case of PDMS, a thin film is formed, bringing gloss and soft feel to the hair shaft [137]. When amodimethicones are exposed to an aqueous environment, some nitrogen atoms will quaternize and bear a positive charge. Because of its keratinic nature, the hair shaft bears a global negative charge when wet, especially if it is damaged. This generates an electrostatic interaction thought to promote deposition and anchorage of the polymer, thus enhancing conditioning.

Other types of silicones are used in hair care. Volatile silicones can be incorporated to reduce drying time in some rinse-off applications like shampoos [138], thus limiting the need for hair dryers and the resulting heat damage to the hair shaft. Silicone resins have been proven to enhance hair volume [139], while silicone polyethers are used in hair styling products to help confer optimized form to hair [140].

In antiperspirants, which typically contain aluminum salts as the active, low molecular weight cyclic silicones are used as carriers, thanks to their volatility and noncooling perception, which leads to a dry feel. They also help prevent salt transfer and cloth staining, a problem associated with mineral oil based products. These cyclic silicones have allowed the development of new product forms such as roll-ons, providing alternatives to CFC-based aerosol formulations [135].

In hygiene applications, the amount of foam is an important parameter, as a shower gel producing a generous foam will be better perceived by the consumer [136]. Due to their amphiphilic nature, silicone polyethers can impact the water-air interface of the foam

structure, resulting in an increase in volume or a stabilization of the foam generated by the cleansing surfactants of the formulation. Some of those polymers also have been shown to reduce the eye irritancy that can be produced by such anionic surfactants.

Silicones and Skin Feel

One of the main reasons skin care formulators incorporate silicones in their formulations is the unique skin feel that silicones confer to cosmetics, which is often described as smooth, silky, elegant or luxurious. Silicones combine an array of properties (low coefficient of friction, liquid at high molecular weight, low surface tension) that impart a perceptively positive feel on skin [141].

Skin feel is a complex phenomenon affected by many variables, so it is difficult to characterize theoretically. A common way to assess sensory properties for a product is to perform sensory panel tests, where a set of trained panelists assess and characterize sensory parameters. Such evaluations confirmed that parameters such as stickiness, gloss, residue, tackiness, oiliness, greasiness and waxiness were almost never cited by panelists evaluating low molecular weight polydimethylsiloxanes, while spreadability and smoothness were often mentioned [141].

Skin feel is impacted by silicone structure. Increasing the length of the chain leads to silicone gums, which have been characterized as giving a velvety feel. Cross-linked silicone elastomer dispersions exhibit a further differentiated feel, which can be described as silky or powdery.

Volatility of Silicones

Low molecular weight silicones are characterized by their high volatility, which influences sensory properties. These materials leave no residue on skin, providing a light feel, which is dependant on the relative volatilities of the silicones considered. Because of their low heat of evaporation (when expressed per gram), they do not need significant heat from the skin to evaporate and consequently do not create the strong cooling effect experienced with water or ethanol-based formulations (see Table 16). This property is particularly sought after in many applications such as antiperspirants, where low molecular weight silicones provide a differentiated dry effect upon use.

Table 16. Heat of Vaporization for Some Volatile Fluids Used in Cosmetics

<i>Fluid</i>	<i>Heat of vaporization</i> <i>kJ/kg</i>
PDMS, cyclic (DP = 4)	172
PDMS, cyclic (DP = 5)	157
Hexamethyldisiloxane	192
Ethanol	840
Water	2257

Permeability of Silicones

PDMS polymers exhibit high permeability to gases. A noteworthy particularity is that this permeability is rather independent of their degree of polymerization, contrary to hydrocarbons (mineral oil vs. petrolatum). Neither does structure type (e.g., linear polymers vs. three-dimensional networks) significantly impact permeability. Table 17 gives comparative data for different families of silicones.

Table 17. Permeability Data for Some Volatile Fluids Used in Cosmetics

<i>Fluid</i>	<i>Water vapor permeability</i> <i>g/m²/h</i>
PDMS, cyclic (DP = 5)	155.7
PDMS, linear (12,500 cSt)	107.4
Silicone gum	148.6
Silicone resin	110.5
Mineral oil	98.0
Alkylmethylsiloxane (C30+)	1.4
Petrolatum	1.3

Permeability is linked to both solubility and diffusion coefficient. Silicones are permeable because they have a relatively high solubility for a number of gases and also exhibit high gas diffusion rates compared to other common polymers. This last characteristic stems from their low intermolecular forces [142].

This behavior is of particular interest for skin creams as it means a silicone film will let water vapor from the dermis and epidermis evaporate and so let the skin “breathe.” In personal care, this property is called “nonocclusivity” and is desirable for products such as body lotions, which are applied to large areas.

However, occlusivity can be increased by substituting methyl groups along the siloxane backbone by longer alkyl groups, thus retaining skin hydration and plasticisation. Surprisingly, aesthetic properties are retained to a great extent [135-142]. Controlled moisturization can be obtained by varying the grafted alkyl group length or the degree of substitution on the polysiloxane chain [142].

17. Medical Applications

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Silicone materials celebrate 60 years of use in medical applications. Quickly after their commercial availability in 1946, methylchlorosilanes were described to treat glassware to prevent blood from clotting [143]. At the same time, Dr. F. Lahey implanted a silicone elastomer tube for duct repair in biliary surgery [144]. Since these pioneers, the interest for silicones in medical applications has remained because of their recognized

biocompatibility. Silicones are used today in many life-saving medical devices like pacemakers or hydrocephalic shunts [145]. Silicones are also used in many pharmaceutical applications from process aids like tubing used to manufacture pharmaceuticals, to excipients in topical formulations or adhesives to affix transdermal drug delivery systems [146]. They also have found use as active pharmaceutical ingredients in products such as antacid and antiflatulent formulations [147-148].

Polydimethylsiloxanes and Biocompatibility

In medical devices and pharmaceutical applications, silicones are used because of their biocompatibility in a wide variety of physical forms. These forms range from volatile and low oligomers to high molecular weight polymers with viscosities from 0.65 cSt to 20×10^6 cSt to viscoelastic compounds and cross-linked elastomers.

Biocompatibility is defined as “the ability of a material to perform with an appropriate host response in a specific situation.” [149-150]. The impact of the biomaterial on its host environment is assessed according to approved standards (e.g., ISO 10993, USP and European monographs) aligned with the performance requirements for the intended applications. Overall, medical grade silicones, and in particular PDMS fluids or PDMS-based elastomers, satisfy the criteria of the above standards, including nonirritating and nonsensitizing behaviors, which explain their wide use in personal care and skin topical applications. A long history of use in medical devices, including long term implants, has made silicones widely recognized as biocompatible. These standards are yet addressing the impact from the host on the foreign material to a lesser extent, as data on biodurability are difficult to acquire. But again, silicones perform well as demonstrated by studies on PDMS-based elastomers explanted and showing good biodurability (Table 1, page 704 in [145])

Silicones with side-chain groups other than methyl (Me) are less used; PDMS polymers are the “preferred material,” even if some unlisted non Compendia/non Pharmacopoeia materials are now also well established, (e.g., silicone pressure sensitive adhesives for transdermal systems). Potential improvements with new silicones are hindered by rigid regulatory requirements, and innovation is sometimes limited to the use of current materials in new applications.

Linking physicochemical properties to biocompatibility is not yet fully understood for many materials. Various factors are involved to explain the successful use of PDMS-based materials in medical devices or pharmaceutical applications:

- Because of their backbone flexibility, PDMS materials can preferably expose their low interacting Me group substituents at many interfaces, leading to low surface tension, low surface energy and low intermolecular interactions, resulting in a low overall level of interactions at their surfaces. Therefore PDMS materials are among the most favored polymers when considering biocompatibility [4].
- Their composition is well established. PDMS polymers do not require stabilizers because of their intrinsic stability. PDMS elastomers do not require plasticizers because of their low T_g . Hemocompatibility studies have suggested that silicone tubing may be

superior to PVC tubing [151]. Impurities are well characterized siloxane oligomers and the toxicology profile of these oligomers has been investigated recently in detail (see Section 21). Other impurities are catalyst traces, such as acids or bases used in polymerization, but these are easy to eliminate and usually not an issue. Similarly, traces of platinum catalyst used at very low levels in cross-linking reactions may be present (platinum content 5 ppm to 20 ppm), and again this is usually not an issue. Only some tin catalysts used in room temperature curing materials or byproducts of peroxides used as initiators in some high consistency rubbers (HCR) have raised concerns [145].

Medical Devices and Pharmaceuticals

Apart from their prevailing biocompatibility, other properties contribute to the use of silicones in medical and pharmaceutical applications:

- Because of their low liquid surface tension around 20.4 mN/m and slightly higher critical surface tension of wetting of 24 mN/m, PDMS polymers spread easily to form films over substrates like skin but also spread over their own absorbed film.
- Because of their viscoelastic behavior, resin-reinforced silicones or partially cross-linked elastomers (e.g. gels) have pressure sensitive properties. Their soft, rubbery behavior makes such silicones very appropriate materials for contacting biological tissues by minimizing the risk of trauma at the interface (e.g., low skin stripping force, gentle removability, no adhesion to wound bed). This allows their use in transdermal drug delivery and wound management applications to secure patches or dressings to the skin with minimum impact on the contacting area [152].
- Because of their high permeability, silicones allow the diffusion of many substances such as gases (i.e., oxygen, carbon dioxide, water vapor) but also the diffusion of various actives (i.e., plant extract, drug, or even protein). This explains their use in personal care, skin topical applications or wound dressings (nonocclusive properties, no maceration) [153]. It also explains their use as adhesives or elastomers in controlled drug delivery systems [154-155-156-157].

Another practical aspect should not be ignored. Because of their stability, silicones are easy to sterilize by steam or ETO. Gamma or beta radiation sterilization require more precautions as they can induce radical reactions [158].

Overall, it is often an association of properties that supports the use of silicones in medical applications (see Table 18) [159-160].

Table 18. Correlations between Silicone Materials, Performance and Applications

<i>Silicone Materials</i>	<i>Key Physical Characteristics and Performance</i>	<i>Medical and Pharmaceutical Applications</i>
Fluids - Polydimethylsiloxane - Organofunctional siloxane - Silicone polyether - Silicone alkyl wax	- Spreadability, film-forming - Diluent, dispersing property - Substantivity - Controlled occlusivity - Hydrophobicity - Lubricant property - Emulsifying property	- Siliconization of needles and syringes - Medical device lubrication - Excipients for topical formulations - Skin protecting composition - Drug carrier
Compounds - Silica + polydimethylsiloxanes	- Antifoam - Diluent, dispersing property	- Antiflatulent (APIs)
Gels (unreinforced elastomers) - Cross-linked polydimethylsiloxanes	- Softness - Resilience - Tackiness - Transparency - Adjustable cure conditions: from ambient to elevated temperature - Foamable	- Cushioning material - Gentle adhesive for skin (soft skin adhesive) - Wound interface (nonadherent wound dressing, foam dressing) - Soft matrix for drug release
Elastomers - Cross-linked polydimethylsiloxanes - Reinforced with silica - Various cure system: radical, hydrosilylation, condensation	- Rubbery property - Mechanical resistance - Adjustable modulus - Adjustable cure conditions: from ambient to elevated temperature - Adjustable cross-linking conditions - Foamable - In-situ film-forming	- Soft and resilient material for medical device - Recognized biocompatibility for human implantation (e.g., pacemaker) - Medical adhesive (sealant) - Film-former
Pressure sensitive adhesives (PSAs) - Silicate resin in polydimethylsiloxanes	- Tacky material - Adhesion to skin and various substrates (e.g., plastic films) - Substantive film-forming	- Temporary fixation of devices on the skin (e.g., wig, catheter) - Film-former - Transdermal drug delivery system

Medical Devices. Contradictory to pharmaceuticals, medical devices are articles or associations of articles used in health care to support therapeutic treatments and assist patient life without pharmacological effects and interferences with biological processes. Silicones are used as components or fabricating materials in many such devices.

Silicone fluids are used to lubricate or “siliconize” many medical surfaces like syringe pistons and barrels. The result is reduced “jerk” during injections or on needles, thus reducing pain [143- 161].

Silicone polymers are easily converted into elastomers by creating covalent bonds between adjacent macromolecules to form three-dimensional networks [3]. Various chemical reactions are available to cross-link or cure silicone polymers (see Section 1):

- Condensation cure between hydroxy, alkoxy or acetoxy groups in presence of tin or titanium catalysts, with liberation of water, alcohol or acetic acid and formation of Si-O-Si bonds
- Radical initiated cure and reactions between alkyl and/or alkylene groups using peroxide to form Si-alkyl-Si bonds, but requiring post-cure to eliminate peroxide byproducts
- Addition cure or hydrosilylation of vinyl functional polymers by hydrogen functional siloxanes in the presence of platinum catalyst to form Si-CH₂-CH₂-Si bonds; in many applications, this reaction is preferred (addition reaction without byproducts; low level of Pt catalyst: 5 ppm to 20 ppm as Pt)

Physical properties are adjusted by controlling the cross-linking density and using reinforcing fillers, usually fume silica. Barium sulfate is added when radiopacity is required.

Because cross-linking points are far apart, dimethylsiloxane segments are most likely to be exposed on the surface of these elastomers, so elastomers display the good biocompatibility associated with PDMS fluids.

Various methods are used like casting, molding and injection to produce parts, or extrusion to produce tubing. Applications range from short term, noninvasive devices to critical, long term devices and are as diverse as long term implants like mammary implants (not without controversy), pacemaker leads, peristaltic tubing in heart-bypass machines or hydrocephalus shunts for regulating cerebrospinal brain fluid (see Figure 31) [145-162-163-164].

Silicone coatings (solvent-based elastomer dispersion) are also used over other materials like natural latex to reduce adverse effects (see Figure 32).



Figure 31. Long term implant: silicone elastomer valve and tubing of a hydrocephalic shunt (Picture courtesy of Medos, a Johnson & Johnson company).

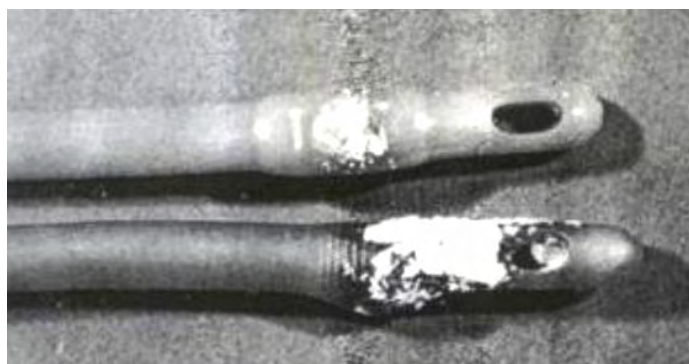


Figure 32. Short term implant: comparison of the incrustation on a silicone-coated latex catheter (top) vs. a latex catheter (bottom) (Picture courtesy Dow Corning).

Silicone gels, adhesives and foams are part of various wound dressings used to reduce nursing costs, but also to improve comfort and therapy [165]. Silicone gels in particular have been successful in this case. These soft, relatively cohesive and tacky gels are platinum-cured elastomers without reinforcing fillers and are used:

- As filling materials in cushions to prevent pressure sores
- In wound dressings because of their permeability to oxygen and water vapor (no maceration dressing), with gentle adhesion to skin around a wound, but with nonadherence to damaged tissues and the healing wound bed
- In scar treatment where a dressing such as silicone gel sheeting has demonstrated its efficacy for the treatment of keloid and hypertrophic scars, as confirmed by various studies including a meta-study [166-167].
- More recently, the release of actives from adhesives has been investigated with enzymes for the debridement of necrotic tissues [153].

Pharmaceutical Process Aids. Silicones are commonly used as process aids in the production of pharmaceuticals like:

- Silanes as temporary protective agents in the synthesis of complex molecules such as antibiotics (e.g., penicillin or cephalosporin). Specific groups are protected by silylation

(e.g., carbinols reacted with trimethylchlorosilanes to form a Si-O-C bond later easily hydrolyzed to recover the active molecule) [168-169]

- Antifoams in fermentation process (see Section 3)

- Silicone tubing used to prepare drugs or vaccines in various fluid transfer operations, peristaltic pumping and filling operations. This tubing helps reduce investment costs in fixed stainless steel lines and, particularly for single-use applications, to eliminate costs associated with validation of cleaning-in-place (CIP) or sterilization-in-place (SIP) and disposal of contaminated waste waters [170-171-172]. Innovative biotech processes take advantage of silicone elastomer properties such as their gas permeability in fermentation cell systems, in which the oxygenation is directly achieved via gas permeation through the silicone tubing wall [160].

Pharmaceutical Ingredients. Silicones are present in many pharmaceutical finished drug products, and more than 350 products containing silicones are listed in various compendia [173].

Cyclics (Cyclomethicone NF) are used in topical products because of their good spreading and volatility, with low heats of evaporation per gram of formulation (resulting in no cooling effect on the skin) [173].

In the US, silicone fluids (Dimethicone NF) around 1,000 cSt are recognized as skin protectants for use in over-the-counter products [174]. This benefit is exploited in creams and ointments, and is most likely due to the high spreadability and high hydrophobicity of PDMS.

Increasing the molecular weight, using PDMS gums (fluids with viscosity around or higher than 600,000 cSt), leads to interesting film-forming materials that are transparent, long-lasting on the skin and capable of improving the substantivity of personal care ingredients as sunscreens or active pharmaceutical ingredients (APIs) (e.g., ketoprofen) [175].

Polydimethylsiloxanes alone (dimethicone) or compounded with silica (simethicone) are used in gastroenterology for their antifoam properties. They reduce foaming in the stomach without modifying the gastric pH, and are thus used in many antifatulent/antacid products, in particular in countries using hot spices. They are considered an API, but their mode of action is physical; they are not metabolized but excreted as such [176].

Silicone pressure sensitive adhesives (PSAs), which are PDMS/silicone resin networks, are used in numerous transdermal drug delivery systems (TDDS) to fix the drug device onto the skin (see Figure 33) [177]. These are viscoelastic compounds in which the PDMS fluid contributes to the wetting and spreadability of the adhesive and the resin, acting as the reinforcing agent, to the elastic rheological component. Because of the PDMS permeability, these PSAs allow the slow and controlled diffusion of various actives for various treatments: nitroglycerin (angina pectoris), estradiol (hormone

replacement), fentanyl (pain management) and others. Both reservoir and matrix systems are known, the latter often considered because of its greater construction simplicity [177].

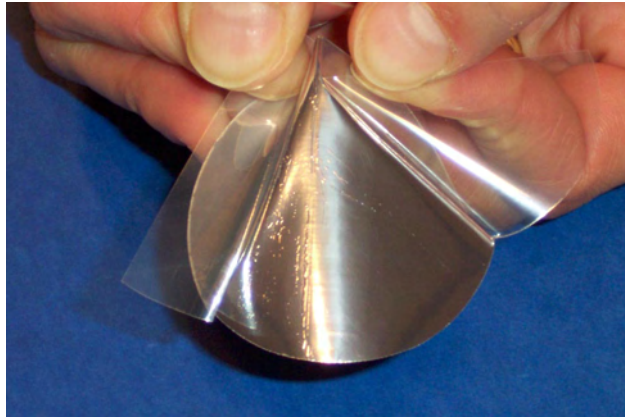


Figure 33. Transdermal drug delivery system or patch with a silicone pressure sensitive adhesive (Picture courtesy Dow Corning).

Silicone elastomers are used in drug-loaded pharmaceutical devices for the release of various APIs such as levonorgestrel in a subcutaneous contraceptive implant or 17 beta-estradiol in a vaginal ring for the treatment of urinary problems associated with menopause. In these reservoir devices, the release of the API is controlled by the permeability of the PDMS cross-linked network [176].

In all the above applications, silicones have been considered because of their contribution to biocompatibility (medical devices), ease of use (pharmaceutical process aids) or improvement of comfort and/or treatment, allowing lower and local dosage forms with fewer side effects or making wound dressings easier to apply for potentially better compliance [177].

18. Silicone Lubricants in Industrial Assembly and Maintenance

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In this industrial segment, silicones are used as sealants (see Section 8) or lubricants. Lubricants will therefore be the focus of this section. Silicone lubricants are not limited to assembly and maintenance, as they are also used in other industries like the automotive, chemical or food industries.

Historically, silicones have been used as lubricants right from the start of the industry in the form of a silica-thickened PDMS compound, which is sometimes referred to as a “noncuring sealant,” and well known to chemists as “vacuum grease” for lubricating glassware joints [178]. This application highlights the properties of silicones that make

them superior to other lubricating liquids in some applications; for example, their possible use over a wide range of temperatures from synthesis at low temperatures as with liquid ammonia to distillation under vacuum at high temperatures.

Tribology and Lubrication Mechanism

Tribology is the engineering discipline that studies the friction and wear phenomena occurring between two moving surfaces in contact with each other as well as the mechanism of lubrication.

Friction is physically characterized by the coefficient of friction and as the ratio of the force required for moving two surfaces to the applied force perpendicular to the moving direction. Friction consists of an adhesive and a destructive component. The later results in wear of various forms [179]. Coefficients of friction range from 0.0001 to 0.0005 for air bearings as used in dental drills up to 0.3 to 0.5 for automotive brake systems.

Lubrication is basically a reduction of both wear and friction by generating a lubricating film between the moving surfaces. There are three modes of lubrication characterized by the ratio of lubricating film thickness to the sum of both surfaces' roughness:

- Boundary lubrication, when the ratio is smaller or equal to 1, and when the surface asperities interfere with each other resulting in a high coefficient of friction
- Mixed lubrication, when the ratio is between 1 to 5, and when the surface asperities occasionally interfere with each other due to load variation
- Fluid film lubrication, when the ratio is larger than 5, and when a complete separation of the two moving surfaces is achieved, resulting in a low coefficient of friction

The generation of a fluid lubricating film can be achieved by pressurizing the lubricating fluid via an external pump as done for turbine start-ups, but this is an exception. In the majority of fluid film lubrication, the geometries are designed in such a way that the necessary pressure is built internally within the fluid itself by the velocity of the surfaces in movement. The velocity profiles in the lubricating contact zone are a combination of Couette's flow with linear velocity distribution and Poiseuille flow with a parabolic velocity distribution. The fluid flow is forced through a wedge that generates a pressure profile according to Bernoulli's law. The pressure generation is similar to that of aircraft wings. In this analogy, one can compare the change from mixed to fluid film lubrication with the takeoff of an airplane, which is the minimum of the curve in Figure 34 (see further) [180].

So, the concept of lubrication is to separate two moving surfaces with a "softer and easier-to-shear" liquid material or lubricant located between the surfaces, and to build up enough pressure in the liquid to separate the two moving surfaces and reduce the coefficient of friction or the force needed to move them against each other under an applied load. As seen in Figure 34, at low speeds the lubricant does not have sufficient internal pressure to separate the two slow-moving surfaces, resulting in high friction. As speed increases, the internal pressure induced by shear in the lubricant separates the two moving surfaces and brings the coefficient of friction to a minimum. At higher speeds, the coefficient of friction increases again due to the work required to shear the lubricant.

Figure 34 also shows that for lubricants of similar composition but of different viscosities, the higher the lubricant viscosity, the earlier surface separation or lubrication occurs, and also that optimum performance is therefore a function of the applied shear, or a corresponding rotational speed in many cases.

This shows that successful lubrication depends on the selection of the most suitable fluid vs. the particular application conditions like speed as well as load, environmental aggressions and temperature.

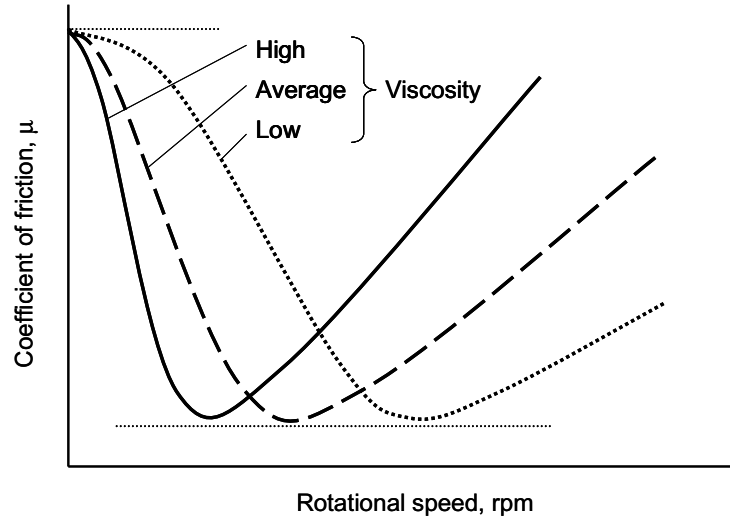


Figure 34. *Coefficient of friction vs. rotational speed in a journal bearing, a plain bearing without rolling parts. Picture courtesy Dow Corning GmbH.*

Polymeric Lubricant Composition

Among various liquids, polymeric materials have come out as the best option for lubrication. If considering the Mendeleev table, only two elements are liquid at room temperature, bromine and mercury, but neither is suitable as a lubricant (due to reactivity and toxicity). As liquid, water also comes to mind. But even though water has good lubricating properties as demonstrated by floating movements of boats and various ice compressing forms of movement, the limitation is that water is only available in one single and low viscosity, and it is liquid only in a narrow range of temperatures; not to mention its corrosiveness that further precludes its use as a lubricant. Actually, the same holds true for many other low molecular weight chemical species.

So, this explains why lubricating fluids are mostly polymeric in nature; for example, organics such as mineral oil based fluids with various degrees of paraffinic, naphthenic or aromatic content. Or, they may be synthetic fluids like poly alpha olefins, neopolyol esters, polyalkylene glycols, dibasic esters, phosphate esters, polybutenes, dialkylbenzenes and perfluorinated polyethers, as well as silicones like PDMS [181].

Because of their low Me-to-Me intermolecular interactions and high backbone flexibility, PDMS materials have a low T_g and are liquid at room temperature, even if of high

molecular weight. PDMS materials have high boiling points, and their viscosity is less affected by temperature changes than organics. These properties make PDMS polymers interesting as possible lubricants. Yet as their surface tension is low, they tend to spread on surfaces more than organic lubricants.

High spreading and high compressibility limit the internal pressures than can build within PDMS materials when used as lubricants and limit their load-carrying capacity if compared to organic lubricants of the same initial viscosity.

Today, three types of silicones are used as lubricants in industrial assembly and maintenance applications:

- Dimethyl siloxane polymers (PDMS, known as dimethyl silicone)
- Phenylmethyl dimethyl siloxane copolymers with phenyl substitution from 10 to 90% (known as phenyl silicone)
- Trifluoropropylmethyl dimethylsiloxane copolymers (known as fluorosilicone)

Silicones, like mineral oils and most synthetic lubricant fluids, are also compounded with thickeners such as metal fatty acids to give lubricating greases capable of keeping the lubricating fluid in close contact with the surfaces in movement. The thickener can be pictured as a sponge that holds the lubricating fluid in place, and such greases are used when total sealed enclosure is not possible. The fluids are further formulated with additives to improve the physical properties of the fluid itself or to add capabilities for mixed and boundary lubrication. Such formulations still represent a challenge for silicones beyond fluid film applications; the range of available additives is limited because these additives were tailored for organic-based materials.

Examples of Silicone Lubricant Applications

Each lubricant application is characterized by its specific operating conditions, which are load, environmental aggressions, temperature and speed.

Load is a limiting factor for silicone lubricants, particularly in metal-to-metal lubrication; so when other conditions require a silicone lubricant, the dimensions of the lubricating contact surfaces may need to be increased. Fluorosilicone lubricants have higher load-carrying capacity due to their higher adhesion to metal substrates. However, for all metal-to-plastic or plastic-to-plastic combinations, silicone lubricants have sufficient load-carrying capacity.

Environment aggressions have less effect on silicones if compared to organic lubricants. The oxidation resistance of silicones makes them suitable for long-life applications. Because of their inertness to most chemicals, silicone lubricants are widely used in the chemical industry, and also in food and beverage processing. Though the load-carrying capacity makes silicones a candidate for plastic lubrication, it is their inertness with almost all plastics or elastomer materials that makes them ideal in these applications. Poor compatibility is experienced only when silicones have to lubricate silicone elastomer surfaces because of the swelling they induce in the silicone elastomers.

Temperature capability of silicone-based lubricants is unsurpassed as covering the widest range.

Speed or better “high shear by design” is required for silicone lubricants in metal-to-metal applications so as to generate enough internal pressure and load-carrying capacity. For plastic lubrication and when using a fluorosilicone lubricant, lower speeds are possible.

Table 19 compares the three types of silicones used as lubricants vs. organics [182].

Table 19. Silicone Lubricant Properties vs. Those of Organics

<i>Lubricant</i>	<i>DP (*)</i>	<i>MW Da</i>	<i>Viscosity at 40 °C cSt</i>	<i>Pour point °C</i>	<i>Flash point °C</i>
Poly alpha olefine (PAO)	20 - 60	150 - 450	5 - 50	-63 to -57	165 - 258
Perfluorinated polyether (PFPE)	10 - 180	1100 - 13,000	4 - 500	-90 to -30	n.a.
Dimethyl silicone	20 - 1,300	1,500 - 100,000	15 - 45,000	-60 to -41	230 - 316
Phenylmethyl silicone	70 - 500	5,600 - 40,000	40 - 700	-73 to -13	275
Fluorosilicone	40 - 100	5,000 - 10,000	150 - 5,300	-47 to -32	260 - 316

* DP: degree of polymerisation

Practical examples are given in Figure 35 through Figure 38 [183].

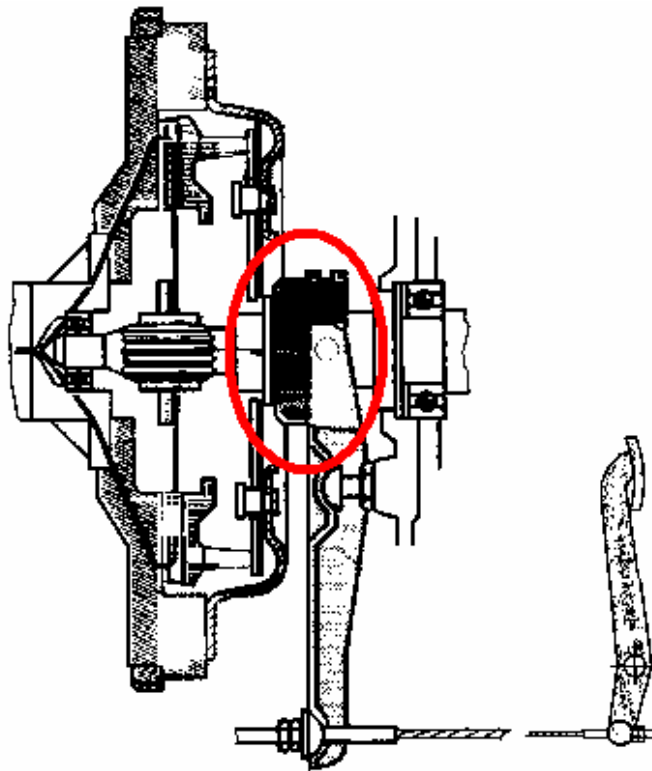


Figure 35. Clutch release bearing with a phenyl silicone grease, which has wide temperature capabilities. Picture courtesy of Dow Corning GmbH.

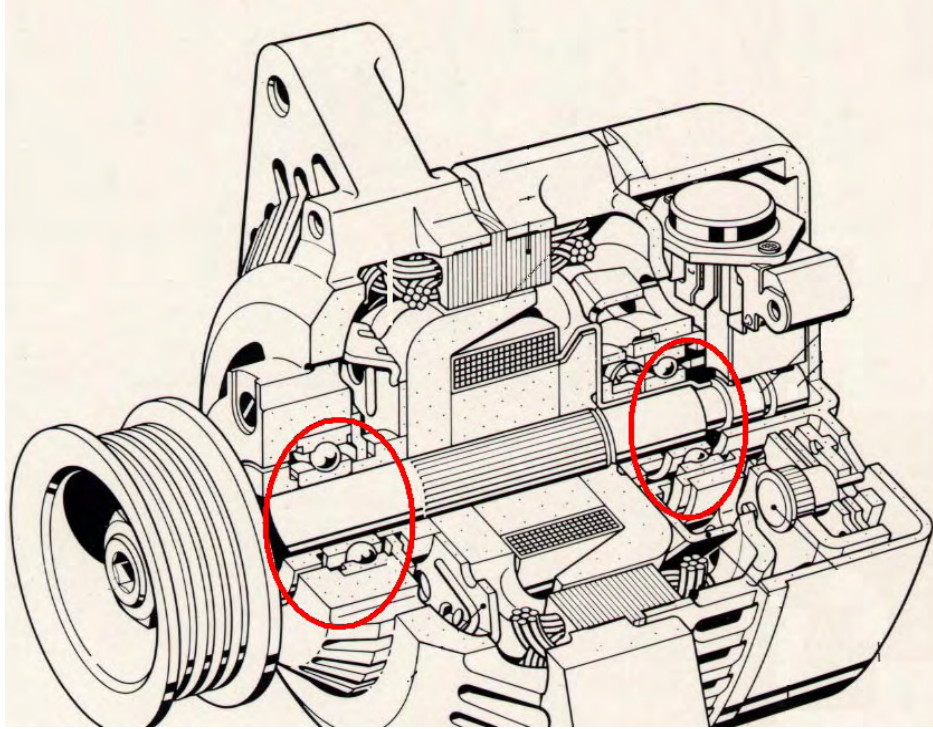


Figure 36. *High power alternator and bearings lubricated with a fluorosilicone grease, which offers resistance to high temperatures. Picture courtesy of Dow Corning GmbH.*

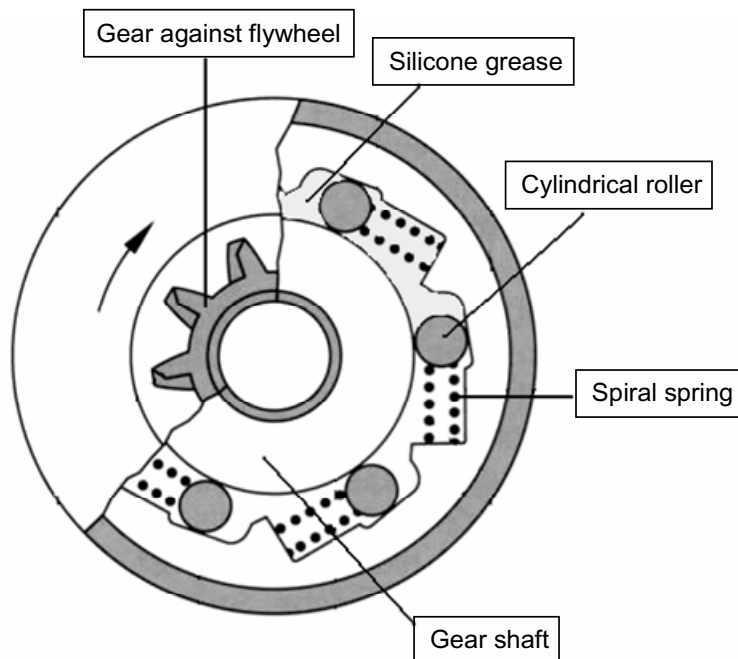


Figure 37. *Starter motor with silicone grease lubricant, which provides wide temperature capabilities and a high coefficient of friction to allow decoupling and prevent slippage. Picture courtesy of Dow Corning GmbH.*

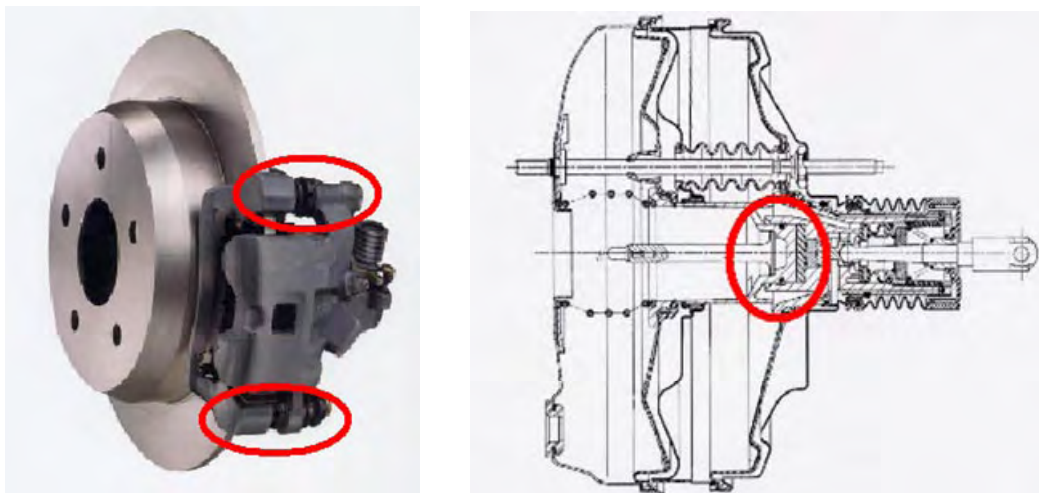


Figure 38. Brake systems (right to left, calliper guides and brake booster) with silicone lubricants, which give wide temperature capabilities and compatibility with plastics and elastomers. Pictures courtesy of Dow Corning GmbH.

19. Organo-Functional Silanes

F. de Buyl, Dow Corning Europe SA, Seneffe (Belgium)

The synergy between organic and silicon chemistries has been investigated for more than 50 years, and has led to the development of many organo-functional silanes that are essential today in many applications [184-185-186].

Monomeric silicon chemicals are known as silanes. A silane that contains at least one silicon-carbon bond (e.g., Si-CH₃) is an organosilane. The carbon-silicon bond is very stable and nonpolar, and in the presence of an alkyl group it gives rise to low surface energy and hydrophobic effects.

Organo-functional silanes are molecules carrying two different reactive groups on their silicon atom so that they can react and couple with very different materials (e.g., inorganic surfaces and organic resins via covalent bonds and often via a polymeric “transition” layer between these different materials).

The value of organo-functional silanes as coupling agents was discovered in the 1940s, during the development of fiberglass-reinforced composites [184].

When initially fabricated, these new composites were very strong, but their strength declined rapidly during aging underwater. This weakening was caused by a loss of bond strength between the glass fibers and the resin. Researchers found that certain organo-functional silanes prevented ingress of water and bond displacements at the fiber/resin interface but also significantly increased the composite initial strength (see Figure 39).

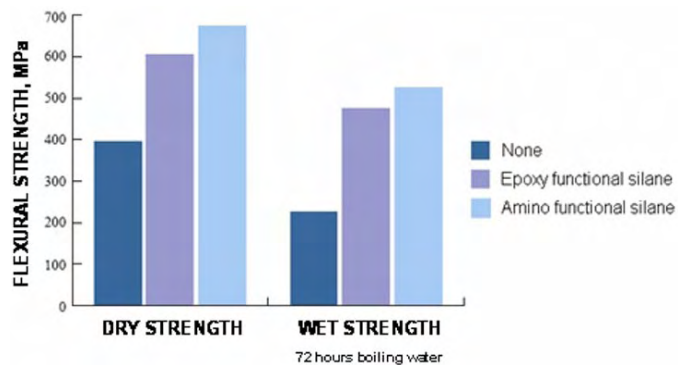
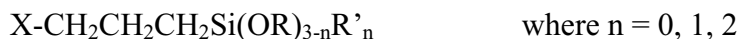


Figure 39. Effect of silane coupling agents on the strength of glass-reinforced epoxy.

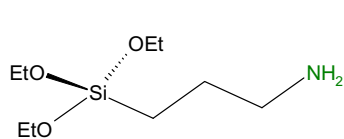
Other applications were later discovered for such silanes, like the treatment of fillers to increase reinforcement, as additives in inks, coatings and sealants to improve adhesion or in plastics and rubbers to allow for cross-linking.

Chemistry of Coupling with Organo-Functional Silanes

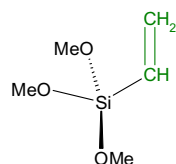
Organo-functional silanes have the following typical molecular structure:



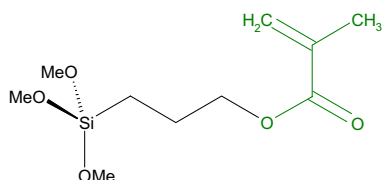
Many combinations are possible, but these are characterized by the fact that they contain two different types of reactive groups. The OR groups are hydrolyzable groups such as methoxy, ethoxy or acetoxy groups. The group X is an organo-functional group, such as epoxy, amino, methacryloxy, or sulfido. The presence of some Si-alkyl groups ensures low surface tension and good wetting properties (see Figure 40).



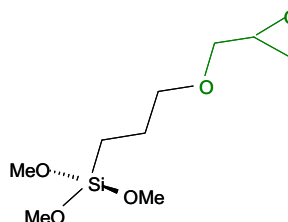
Amino-silane
γ-Aminopropyltriethoxysilane



Vinyl-silane
Vinyltrimethoxysilane



Methacryloxy-silane
γ-Methacryloxypropyltrimethoxysilane



Epoxy-silane
γ-Glycidoxypropyltrimethoxysilane

Figure 40. Examples of organo-functional silanes showing the two different functionalities available for reaction on the Si atom: hydrolyzable alkoxy groups and organic-functional group.

The Si-OR bonds hydrolyze readily with water, even if only with moisture adsorbed on the surface, to form silanols Si-OH groups. These silanol groups can then condense with each other to form polymeric structures with very stable siloxane Si-O-Si bonds. They can also condense with metal hydroxyl groups on the surface of glass, minerals or metals to form stable Si-O-M bonds (M = Si, Al, Fe, etc...). This allows surface treatment, coupling and assembling of very dissimilar surfaces chemically, as between inorganic and organic materials (see Figure 41).

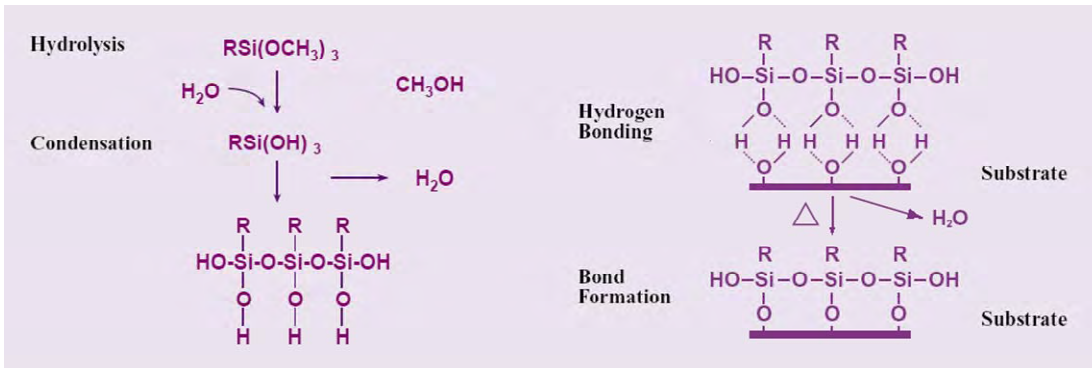


Figure 41. Organo-functional silane hydrolysis, condensation and covalent bonding to an inorganic substrate.

The organo-functional silane concentrations used here are such that more than a monolayer is being built at the interface. A tight polymeric siloxane network is created on the inorganic filler or metal surface, which becomes more diffuse into the adjacent organic resin.

The properties of the organo-functional silane should match the reactivity of the resin with appropriate groups on the silane to react with the resin (e.g., epoxy or amino groups to react with epoxy resins, amino groups to react with phenolic resins or a methacrylate group to react with styrene in unsaturated polyester resins). But also the organo-functional silane should match the solubility parameter of the adjacent resin to ensure a smooth transition at the interphase. The formation of an interpenetrating network (IPN) at the boundary interphase appears essential and probably also explains the improved adhesion observed with thermoplastic polymers (see Figure 42) [187-188].

Organo-functional silanes have shown greatest benefits in three areas: mineral filler treatment, cross-linking and as adhesion promoters.

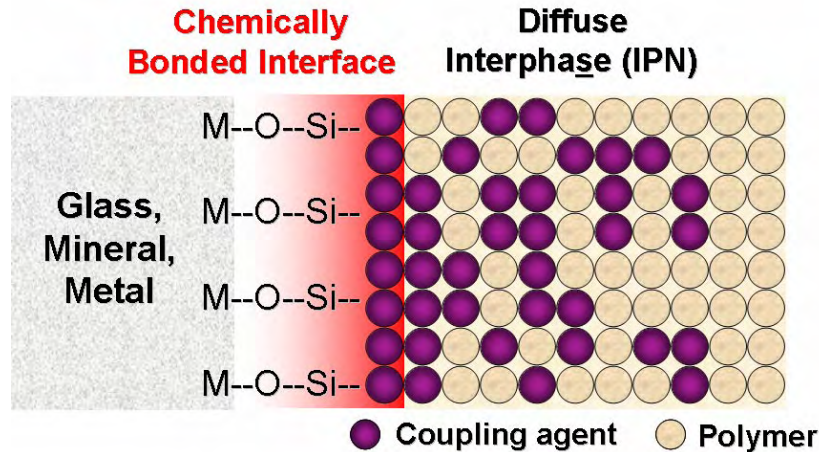
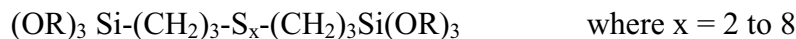


Figure 42. IPN structure created by an organo-functional silane at the interphase between an inorganic glass, mineral, metal substrate ($M = \text{Si}, \text{Al}, \text{Fe}, \dots$) and an organic polymer.

Mineral Filler Treatment. Mineral fillers have become increasingly important modifiers for reinforcing organic polymers, thermoplastics or thermosets. Yet, the metal hydroxyl groups on the mineral filler surface are hydrophilic, and this translates to incompatibility with organic polymers. Organosilanes are ideal for treating the filler surface, making the filler more compatible and easier to disperse in the polymer. Any minerals with silicon or aluminum hydroxyl groups on their surfaces (e.g., silica, glass bead, quartz, sand, talc, mica, clay or wollastonite) can be treated with organo-functional silanes. These will ease dispersion of the fillers and improve wetting by, and adhesion to, the polymer. This results in lower filler/polymer mix viscosities and improved mechanical properties [189].

A typical example is the sulfido-silanes:



Selecting the adequate sulfido-silane enables surface treatment of the silica used in green tires and bonding to organic rubber, which was proven extremely effective for optimizing the viscoelastic and mechanical properties of the silica-rubber composite for “more miles per gallon.”

Cross-Linking. Polymers and polymeric composites are becoming increasingly attractive as engineering materials. They are highly competitive compared to metal or metal alloys due to their low cost and low density, ease of compounding using extrusion or injection molding processes, and inherent lack of corrosion-related problems.

One way to improve performance of such plastics is to cross-link them to some degree. One well-known example using organo-functional silanes is the cross-linking of polyethylene to give partially cross-linked polyethylene or PEX [190-191]. This is achieved by grafting vinyl-functional alkoxy silanes on the PE chains using peroxide as an initiator. The vinyl groups allow for grafting on the PE backbone, and the alkoxy groups allow for subsequent cross-linking between the PE chains upon exposure to heat

and moisture. The main applications are for piping of various kinds (e.g., under floor heating, drinking water) and wire and cable insulation.

Similarly, cross-linking is used to enhance mechanical properties in thermoplastic vulcanisates (TPVs), through dynamic vulcanization process and where the silanes play many roles: cross-linker, adhesion promoter and even intermediate to generate in situ filler.

Adhesion Promoter. Organo-functional silanes are known for surface modification. So as additives, they can enhance adhesion between dissimilar materials because of their low surface tension (which ensures good surface wetting), their reactivity to different surfaces and their ability to create interactions and make an adequate transition interphase between the adhesive layer and the substrate to bond [186-192-193].

Trends and Perspectives

Today, there are two major trends:

- The optimization of organo-functional silane molecules and conditions for processing them, aiming to reduce emissions of volatile organic compounds (VOCs)
- The design of new and sustainable composite materials with improved end-user benefits, taking advantage of the wide variety that commercially available silanes or those under development offer in terms of functionalities, reactivities and processing flexibility at relatively mild conditions.

Low VOC Silanes and Processes. Conventional organo-functional silanes rely on the hydrolysis of their Si-OR groups and subsequent condensation for their coupling with inorganic surfaces or cross-linking within plastic matrices. Human health and environmental concerns are leading to the development of new products with less hydrolysis/condensation byproducts such as hydrolyzed, lower alkoxy-containing intermediates or solventless products. Prehydrolyzed silanes under well controlled conditions [194-195], water-based silane solutions, or solid carrier supported silanes that could be added during plastic extrusion, and plasma surface treatment in presence of silanes are among the approaches currently investigated to address VOC issues.

Design of New Materials. Sustainable composites that exploit the reinforcement properties of natural fillers like cellulose are being developed, in which silanes are considered to “manage” the highly hydrophilic nature of the surfaces of such fillers to improve compounding and load transfer to the surrounding plastic matrix [196-197].

Sol-gel processes refer to the polymerization in aqueous or organic medium of metal alkoxides into a monolithic gel via the formation and growth and/or network extension of discreet nanoparticles [198]. As such, traditional materials generated via sol-gel process include stable silica sol and colloids [199], thin films and coatings, composites such as ceramics generated by specific drying conditions of aerogels or xerogels [200], fibers, porous gels and membranes [201]. The potential added properties sol-gel materials bring to plastics in general therefore encompasses a wide variety of properties, including

antigraffiti, antimicrobial, antifouling, anticorrosion [202], optical, protective, adhesive or anti-adhesive, mechanical, dielectric [203], and reinforcing.

20. Plasma and Silicones

S. Leadley, Dow Corning Plasma Solutions, Midleton (Ireland)

The use of plasma in conjunction with silicones is a new application field that allows interesting surface modifications.

The term “plasma” covers a broad range of systems whose density and temperature vary by many orders of magnitude. Some plasmas, particularly those at low pressure (e.g., 100 Pa) where collisions are relatively infrequent, have their constituent species at widely different temperatures and are called “nonthermal equilibrium” plasmas. In these nonthermal plasmas the free electrons are very hot with temperatures of many thousands of Kelvin (K), whilst the neutral and ionic species remain cold. Because the free electrons have almost negligible mass, the total system heat content is low and the plasma operates close to room temperature, allowing the processing of temperature-sensitive materials, such as plastics or polymers, without imposing a damaging thermal burden onto the sample. However, the hot electrons create, through high energy collisions, a rich source of radicals and excited species with a high chemical potential energy capable of profound chemical and physical reactivity. It is this combination of low temperature operation plus high reactivity that makes nonthermal plasma technologically important and a very powerful tool for manufacturing and material processing.

These properties provide a strong motivation for industry to adopt plasma-based processing, and this move has been led since the 1960s by the microelectronics community, which has developed “low pressure glow discharge plasma” into a high technology engineering tool for semiconductor, metal and dielectric processing. The use of plasma to deposit thin dielectric films is often referred to as plasma-enhanced chemical vapour deposition (PECVD) processing.

Various precursors are available, specifically designed for the deposition of thin film dielectrics via PECVD and compatible with copper dual damascene and aluminum interconnect processes. These precursors are:

- Gases like Me_3SiH , which can be used with processing technology developed for silane-based dielectric film deposition
- Liquids like Me_4Si , $(\text{SiHMeO})_4$ and $\text{SiMe}_2(\text{OMe})_2$, which can be used with processing technologies developed for TEOS-based dielectric film deposition

Typical thin-film dielectrics formed by these precursors include silicon-carbide (a-SiC:H), silicon-oxycarbide (a-SiOC:H) and silicon-nitride (a-SiCN:H). Typical applications include interlevel dielectric, copper diffusion barrier, etch stop, hard mask, low-k interlevel dielectric, gap fill, and passivation.

Vacuum or low-pressure plasma has increasingly penetrated other industrial sectors since the 1980s, offering processes such as polymer surface activation for increased adhesion/bond strength, high quality degreasing/cleaning and the deposition of high performance coatings. However, due to operation at reduced pressure, processing is restricted to batch wise or at best is pseudo-continuous and thus not applicable to in-line production. Therefore, newly developed atmospheric pressure plasmas offer industry open port or perimeter systems providing free ingress into and exit from the plasma region by work-pieces/webs. Hence, atmospheric pressure plasma offers new continuous, on-line processing capability for many industrial sectors, such as textiles, packaging, paper, medical, automotive and aerospace.

The work of Okazaki et al. in the 1980s showed that a stable glow discharge could be readily formed at atmospheric pressure [204-205], which ignited a volume of research and a wide variety of plasma systems that now operate at atmospheric pressure. The early work by Okazaki focused on generating plasmas using helium as the process gas. Later this was extended to include argon and nitrogen. Further developments have produced atmospheric pressure plasmas in a wide variety of gases, including air [206]. The exact conditions employed vary depending upon the gas, electrode geometry and other factors. Typically these ambient temperature atmospheric pressure plasmas are referred to as diffuse dielectric barrier discharge [207], a term generally used to cover both glow discharges and dielectric barrier discharges that are homogeneous plasmas across the width and length of a plasma chamber [208].

Technology is now available to combine unique precursors and their delivery into an atmospheric pressure plasma operating at ambient temperature to achieve deposition. This process is known as atmospheric pressure plasma liquid deposition (APPLD). Such APPLD equipment comes in two configurations:

- Large-area plasma for processing flexible webs such as textiles, nonwovens, paper, films and foils, fibres, thread, yarn or filament
- Jet plasma for processing three-dimensional, rigid sheet materials or material in fibre/filament form

By directly injecting an aerosol of liquid precursor into a homogeneous atmospheric pressure plasma, a thin conformal layer of polymerised coating can be deposited onto a substrate surface that is in contact with the plasma. Typically, these coatings are some tens of nanometres thick. The combination of liquid precursor and diffuse atmospheric pressure plasma ensures that this process retains all the original functional properties of the liquid precursor – even for large, complex molecules. This is a property unique to APPLD, as almost all other atmospheric pressure plasma processes destroy complex precursors (see Figure 43).

This enables tailoring of the surface chemistry with a specific chemical functionality and/or a specific surface response. This surface engineering can be applied to a variety of different substrate classes for a wide range of applications. Thus, advanced surface properties that include biofunctionality, oil repellency and adhesion promotion are now

available from APPLD technology, offering the prospect of plasma processing penetrating a wide range of new, high-value industrial applications.

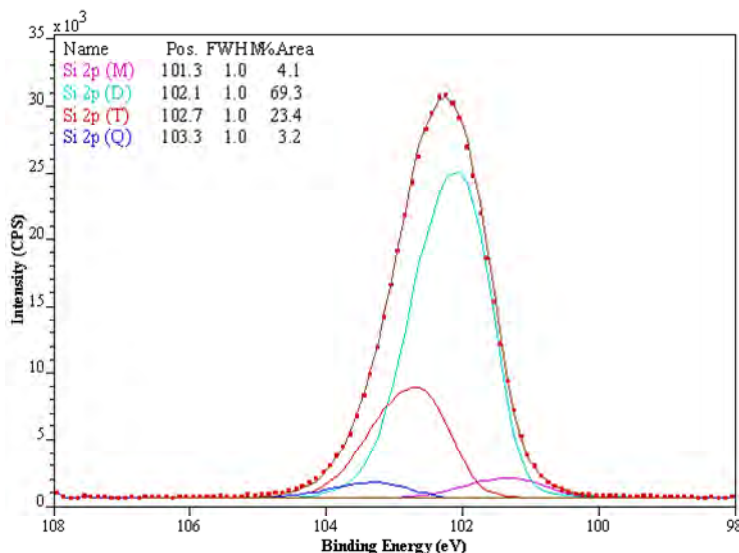


Figure 43. XPS (ESCA) spectra of a polyester film after plasma treatment with a polyhydrogenmethyl siloxane polymer precursor, $M(D^H)_nM$, using the APPLD technology. The presence of peaks corresponding to T and Q units indicate that some modification of the original polymer has occurred, leading to cross-linking. But most of the polymer's original functionality remains as indicated by the strong peak corresponding to D^H units.

Due to the unique nature of the APPLD process, a wide variety of silicones can be utilised as precursors to provide specific surface properties. For example, polydimethylsiloxane (PDMS) polymer coatings are widely used [209] for their excellent hydrophobic properties, which increase water repellency, release and “handle.” Tetramethylcyclotetrasiloxane and octamethylcyclotetrasiloxane have been successfully used as precursors to produce polysiloxane coatings, which have been shown to provide a water contact angle of 140° on a cotton substrate, whereas a water droplet applied to nontreated cotton wets out immediately (see Figure 44).

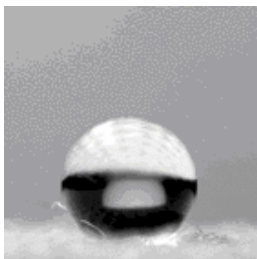


Figure 44. A water droplet on a silicone plasma treated cotton fabric. Picture courtesy of Dow Corning Plasma Solutions.

In oxidising plasma conditions, low molecular weight PDMS precursors are converted to silica-like (SiO_x) coatings. The APPLD process is an alternative route to depositing organosilane molecules, without the requirement of using water or organic solvents.

21. Silicones and Toxicology

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R. Meeks, Dow Corning Corporation, Midland MI (USA)

As described in the previous sections, silicones are used in a wide variety of applications.

These silicones include low molecular weight linear and cyclic volatile oligomers or volatile methyl siloxanes as well as polydimethylsiloxane (PDMS) polymers with viscosities ranging from 10 to 100,000 cSt or higher.

Volatile methyl siloxanes (VMS) like cyclic siloxanes, $(\text{SiMe}_2\text{O})_n$, are widely used in skin care products, in particular the four ($n = 4$) and five ($n = 5$) member cyclics referred to as D_4 and D_5 , respectively [210]. Extensive safety studies conducted on D_4 and D_5 have indicated effects that appear to be rat specific and, therefore, pose little or no risk to human health [211-212]. The effects observed with D_4 include a reduction in litter size and in the number of implantation sites in the uterus and an increase in uterine endometrial hyperplasia and adenomas [213-214-215]. The fertility effects and uterine adenomas occur at the highest vapor exposure concentration achievable without formation of an aerosol (i.e., 700 ppm) and by modes of action that appear to be rat-specific [211-213-216-217]. Exposure to D_5 at the highest achievable vapor concentration of 160 ppm caused an increase in uterine endometrial adenocarcinomas that is presumed to occur by a rat-specific mode of action like D_4 [212-216-218]. Both D_4 and D_5 cause a non-adverse, adaptive increase in liver weight that is considered phenobarbital-like [219-220]. Neither of these materials are mutagenic or genotoxic nor are they immunotoxic [211]. Typically, D_4 and D_5 show around 0.5% and 0.05% dermal absorption, respectively [221-222-223]. Following dermal absorption, >80% of D_4 and >90% of D_5 is eliminated in expired air within 24 hours of exposure [224].

The lowest molecular weight linear material is the highly volatile hexamethyldisiloxane, $\text{Me}_3\text{SiOSiMe}_3$ (HMDS). HMDS has generally shown no significant toxicity. However, recent data have indicated an earlier incidence of testicular tumors in male rats exposed to high levels of material via inhalation [225]. In this same study, there was also an increase in the incidence of kidney tumors in male rats, which have been shown to be mediated through a protein, α -2u-globulin, which is specific to male rats [225]. Other linear molecules of three, four, or five siloxane units have not exhibited hazards in studies to date, though the data are limited for long-term exposure [226]. The materials have very limited absorption via typical exposure routes. Like the higher molecular weight polymers, the low molecular weight linear PDMS materials are not mutagenic, irritating or acutely toxic [226].

The most widely used silicones are the trimethylsilyloxy end-blocked PDMS polymers, $\text{Me}_3\text{SiO}(\text{SiMe}_2\text{O})_n\text{SiMe}_3$, with viscosities between 10 to 100,000 cSt. These materials have shown no toxicity during administration via typical exposure routes, which are either oral or dermal [227]. Due to their high molecular weight, they are neither absorbed from the gastrointestinal tract nor through the skin [228-229]. Following oral ingestion, PDMS is excreted in the feces without modification. *In vitro* studies have not indicated

mutagenic or genotoxic effects. Repeated oral or dermal dosages of different viscosities demonstrated no adverse effects to a variety of mammalian species. Inhalation of aerosols of oily or fatty-type materials, including some kinds of silicones, into alveolar regions of the lung may result in acute toxicity that is likely related to physical disturbances of the lining of the lung with associated effects. There is no evidence of reproductive or teratogenic effects of PDMS from studies conducted with rats or rabbits. Overall, these data show no hazard of PDMS to humans [227].

22. Silicones and their Impact on the Environment

C. Stevens, Dow Corning Europe SA, Seneffe (Belgium)

A large number of studies have been conducted to evaluate the fate and effects of silicones in the environment throughout their life cycle [227]. Releases to the environment from the manufacture of polydimethylsiloxane (PDMS) are strictly controlled and must comply with emission limits specified by regulatory authorities. Subsequently, the environmental fate of silicones depends to a large extent on the nature of the application, the physical form of the material and the method of disposal. Low molecular weight PDMS polymers (< 1000 Da) are primarily used in personal and household care products. High molecular weight PDMS polymers are important as antifoams and lubricants for domestic and industrial use. However, a more important application is as a “solid” silicone such as PDMS-based rubbers or sealants, both of which may be used either in the home (e.g., bath sealants, bake-ware or baby teats) or diverse industrial applications such as textile coatings, electronics, silicone mouldings and rubber gaskets.

“Solid” silicones enter the environment as a component of domestic or industrial waste and will be either land filled or incinerated. In the latter case, they are converted back to inorganic ingredients, amorphous silica, carbon dioxide and water vapour. “Liquid” silicones, both high and low molecular weights, which are used in rinse-off products such as shampoos, hair conditioners or silicone antifoams in detergents, become part of municipal wastewater. The same is true for PDMS used as antifoams in pharmaceuticals. High molecular weight silicones, are virtually insoluble in water, thus, as a consequence of their high binding potential for organic matter, they are effectively removed from municipal wastewater onto the sludge during wastewater treatment. Extensive studies show that more than 95% of silicones are removed from effluents in this way, and that the concentration in discharged effluents borders the level of detection (5 µg/l) [230-231].

The subsequent fate of silicones depends on the fate of the sludge. If incinerated, silicones degrade as indicated above. The other principal outlet for sludge is use as a soil conditioner or amendment. In small-scale field studies, the application of sewage sludge-bound PDMS to soil caused no observed adverse effects on crop growth or soil organisms [232]. Little or no uptake into the plants was observed, which is consistent with animal studies showing that high molecular weight PDMS is too large to pass through biological

membranes of either plants or animals. Extensive studies ranging from small-scale laboratory tests to field studies show that sewage-sludge bound PDMS degrades in soils as a result of contact with clay minerals [233-234-235-236-237-238]. The clay acts as a catalyst to depolymerise the siloxane backbone [238-239]. The primary degradation product, regardless of the PDMS molecular weight, is dimethylsilanediol, $\text{Me}_2\text{Si}(\text{OH})_2$ [234]. Depending on the soil type, this undergoes further degradation either in the soil via biodegradation [239-240] or evaporates into the atmosphere, where it degrades oxidatively via reaction with hydroxyl radicals [241]. Whether degradation occurs in the soil or in the air, there is conversion to inorganic constituents, amorphous silica, carbon dioxide and water.

23. Conclusions

A. Colas, Dow Corning Europe SA, Seneffe (Belgium)

From the above, it can be seen that it is often an association of properties that has led to the successful industrial application of silicones.

In PDMS, an unexpected, highly flexible backbone made of strong and very polar Si-O bonds, but shielded by low interacting methyl groups, leads to low intermolecular forces and properties such as low surface tension, high permeability and low viscosity, together with good chemical and thermal stability.

Some other characteristics contribute to the use of silicones across many industries. The synthesis of PDMS materials does not require heavy metal catalysts or organic solvents. They are made from distilled intermediates and their impurity profile is easy to assess using recent toxicological and environmental studies. Silicone properties can be tailored to applications. The siloxane backbone is easily modified from linear to branched or cross-linked structures or functionalised with groups other than methyl to provide for specific properties.

Notes:

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