

Silicones: Preparation, Properties and Performance

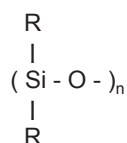
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Abstract

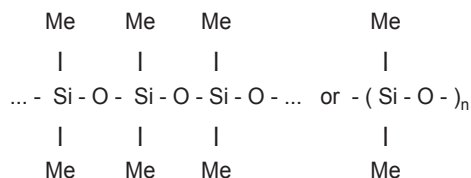
The objective of this article is to give the curious reader a short but scientific overview about the ways silicones are prepared, their key properties and how these properties allow silicones to perform in many different applications.

Introduction

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, with the formulation:



The name silicone was adopted by the industry and usually refers to linear polymers where $R = Me$ or polydimethylsiloxane (PDMS):

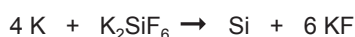


The methyl groups along the chain can be substituted by many other groups (e.g., phenyl, vinyl or trifluoropropyl). The simultaneous presence of “organic” groups attached to an “inorganic” backbone gives silicones a combination of unique properties and allows their use in fields as different as aerospace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

Historic Background

The development of silicone chemistry includes several principal steps.^{1,2}

Silicon was discovered by Berzelius in 1824 from the reduction of potassium fluorosilicate with potassium:



Reacting silicon with chlorine gave a volatile compound later identified as tetrachlorosilane, $SiCl_4$:



The next step was made by Friedel and Craft, with the synthesis of the first silicon organic compound in 1863, tetraethylsilane:



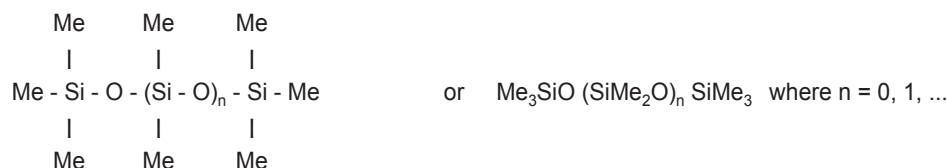
In 1871, Ladenburg observed that, in the presence of a diluted acid, the diethyldiethoxysilane, $(C_2H_5)_2Si(OC_2H_5)_2$, gave an oil that decomposed only at a “very high temperature.”

Kipping laid the foundation of organosilicon chemistry with, among other things, the preparation of various silanes by means of Grignard reactions and the hydrolysis of chlorosilanes to yield “large molecules.” The polymeric nature of silicones was confirmed by the work of Stock.

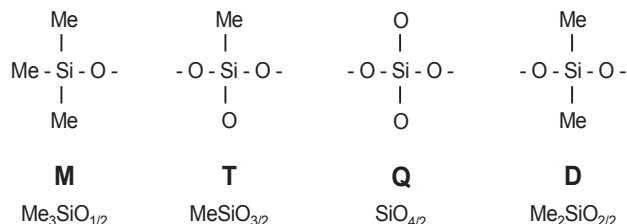
In the 1940s, silicones became commercial materials after Hyde of Dow Corning demonstrated the thermal stability and high electrical resistance of silicone resins, and Rochow of General Electric found a direct method to prepare silicones from Si and MeCl.

Nomenclature

The most common silicones are the polydimethylsiloxanes, trimethylsilyloxy terminated, with the following structure:



These are linear polymers and liquids, even for large values of n . The main chain unit, $-(\text{SiMe}_2\text{O})-$, 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:³



The above polymer 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 $\text{HMeSiO}_{2/2}$).

Note: Confusion is common between silicon (Si, a metallic element), silica (SiO_2 , an inorganic compound) and silicone (a polymeric compound).⁴ Monomeric species are named by substitution based on SiH_4 or silane (a volatile and pyrophoric compound); so Me_2SiCl_2 is named dimethyldichlorosilane.

Preparation: From Sand to Silicones

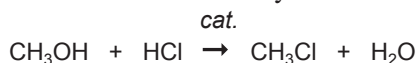
Silicone polymers. Silicone polymers are obtained by a three-step synthesis:

- Chlorosilane synthesis
- Chlorosilane hydrolysis
- Polymerisation and polycondensation

Chlorosilane synthesis. Today, silicones are obtained commercially ($\pm 850,000$ t/y) from chlorosilanes prepared following the direct process of Rochow² and using silicon metal obtained from the reduction of sand at high temperature:



and methyl chloride obtained by condensation of methanol with hydrochloric acid:



The reaction giving chlorosilanes takes place in a fluidised bed of silicon metal powder in which flows a stream of methylchloride, usually at temperatures of 250 to 350°C and at pressures of 1 to 5 bars. A mixture of different silanes is obtained containing mainly the dimethyldichlorosilane, Me_2SiCl_2 .³

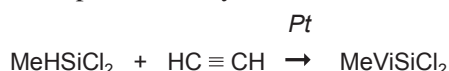
$x \text{ Si} + y \text{ CH}_3\text{Cl}$	$\xrightarrow{\text{cat.}}$		Yield (weight %)	Bp (°C)
		Me_2SiCl_2 [1]	> 50	70.0
		MeSiCl_3	10 - 30	66.4
		Me_3SiCl	< 10	57.9
		MeHSiCl_2	< 5	41.0
		other silanes	5	-

The reaction is exothermic and has a yield of 85 to 90%. A copper-based catalyst is used. The reaction mechanism is not completely understood. Chemisorption phenomena on active sites seem preferred to the radical-based mechanism originally proposed. The various silanes are separated by distillation: as the boiling points are close together, long distillation columns are always seen at silicone factories. The dimethyldichlorosilane [1], which is separated, becomes the monomer for the preparation by hydrolysis of polydimethylsiloxanes (see further). Redistribution reactions can be used to convert the other silanes and increase the commercial yield of the production equipment.⁵

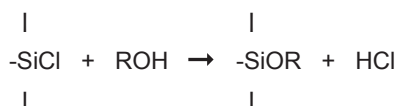
Ethyl- and phenylchlorosilanes can also be obtained through similar reactions to the direct process described above. Phenylchlorosilanes can also be prepared through a Grignard reaction:³



Other chlorosilanes are prepared from an existing silane, e.g., methylvinylchlorosilane is obtained by the addition of methylchlorosilane on acetylene using a Pt complex as catalyst:⁵

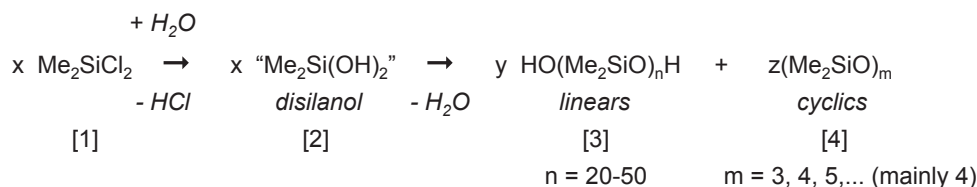


It is also possible to replace the chlorine groups by alcoholysis:



In this way, various silanes with different functionalities can be prepared (e.g., alkoxy and vinyl). These allow coupling reactions to take place between inorganic surfaces and polymers in composite manufacturing.⁶

Chlorosilane hydrolysis. Polydimethylsiloxanes are obtained by the hydrolysis of dimethyldichlorosilane in the presence of excess water according to:³

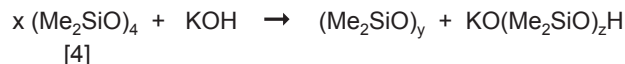


This heterogeneous and exothermic reaction gives formally a disilanol "Me₂Si(OH)₂" [2] which readily condenses, with HCl acting as a catalyst, to give a mixture of linear [3] or cyclic [4] oligomers by inter- or intramolecular condensation. This mixture separates from the aqueous acid phase, the ratio between the two oligomers depending on the hydrolysis conditions (concentrations, pH, solvents).

These oligomers are water-washed, neutralised and dried. The HCl is recycled and reacted with methanol to give the methylchloride used in the direct process described above.

Polymerisation and polycondensation. The linear [3] and cyclic [4] oligomers obtained by hydrolysis of the dimethyldichlorosilane have too short a chain for most applications. They must be condensed (linears) or polymerised (cyclics) to give macromolecules of sufficient length.⁷

Cyclics, (R₂SiO)_m, can be opened and polymerised to form long linear chains, the reaction being catalysed by many acid or base compounds⁵ and giving at equilibrium a mixture of cyclic oligomers plus a distribution of polymers. The proportion of cyclics depends on the substituents along the chain, the temperature and the presence of a solvent. Polymer chain length depends on the presence of substances capable of giving chain ends. For example, in the polymerisation of (Me₂SiO)₄ with KOH, the average length of the polymer chains depends on the KOH concentration:



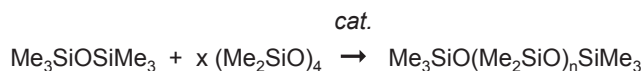
A stable, OH-terminated polymer, $\text{HO}(\text{Me}_2\text{SiO})_z\text{H}$, can be isolated after neutralising and stripping the above mixture of the remaining cyclics under vacuum at elevated temperature. In fact, a distribution of chains with different lengths is achieved.

The reaction can also be made in the presence of $\text{Me}_3\text{SiOSiMe}_3$, which acts as a chain endblocker according to:



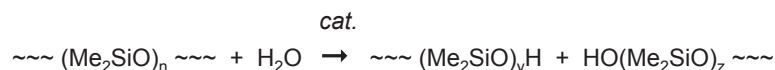
The Me_3SiOK formed attacks another chain to reduce the average molecular weight of the linear polymer formed.

The copolymerisation of $(\text{Me}_2\text{SiO})_4$ in presence of $\text{Me}_3\text{SiOSiMe}_3$ with Me_4NOH as catalyst displays a surprising viscosity change over time.⁷ First, a peak or viscosity maximum is observed at the beginning of the reaction. With such a base catalyst, the presence of two oxygen atoms on each silicon in the cyclics makes them more susceptible to a nucleophilic attack by the catalyst than the silicon of the endblocker, which is substituted by one oxygen atom only. The cyclics are polymerised first in very long, viscous chains, which are subsequently reduced in length by the addition of terminal groups provided by the endblocker, which is slower to react. This reaction can be described as follows:



The ratio between D and M units determines the average molecular weight of the polymer formed.

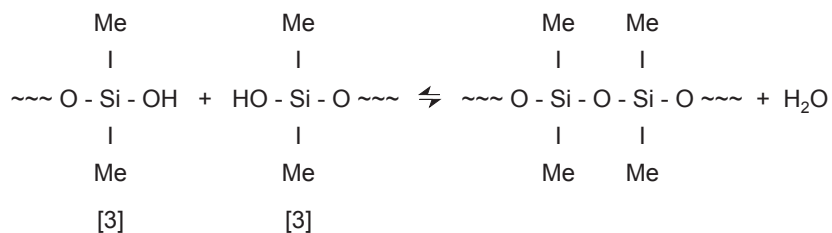
Catalyst removal (or neutralisation) is always an important step in silicone preparation. Most catalysts used to prepare silicones can also catalyse the depolymerisation (attack along the chain), particularly in the presence of water traces at elevated temperatures:



To benefit as much as possible from the thermal stability of the silicone, it is therefore essential to remove all remaining traces of the catalyst. Labile catalysts have been developed, which decompose or are volatilised above the optimum polymerisation temperature. These can be eliminated by brief overheating to avoid catalyst neutralisation or filtration.⁷

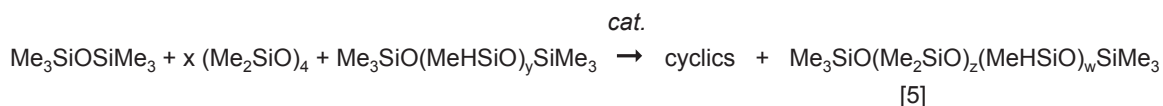
The cyclic trimer, $(\text{Me}_2\text{SiO})_3$, is characterised by an internal ring tension and can be polymerised without re-equilibration of the resulting polymers. With this cyclic, polymers with narrow molecular weight distribution can be prepared, as well as polymers carrying only one terminal reactive function (living polymerisation). Starting from a mixture of different "tense" cyclics also allows the preparation of block or sequential polymers.⁷

Linears can be condensed, a reaction catalysed by many acids or bases:^{5,7}

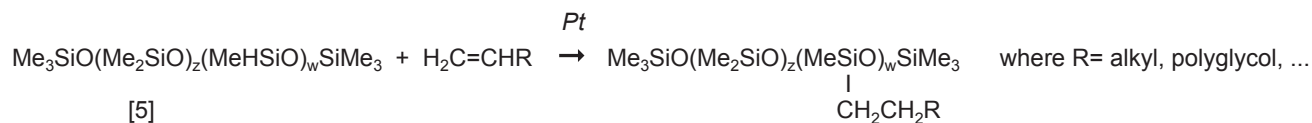


to give long chains by intermolecular condensation of terminal SiOH. A distribution of chain length is obtained, and longer chains are favoured when working under vacuum and/or at elevated temperatures to reduce the residual water concentration. Acid catalysts are more efficient when the organosilanol carries electron-donating groups, base catalysts when it carries electron-withdrawing groups. Some catalysts can induce a redistribution by attacking the polymer chain with the formation of cyclics. This will be important when condensing a mixture of linear oligomers such as dimethyl- and methylphenyl-polysiloxanes. A sequential polymer will be obtained in the absence of redistribution, while a random polymer will result if a catalyst capable of opening the main chain is used.

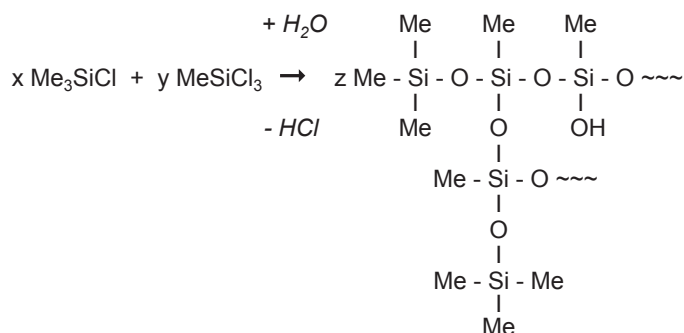
Apart from the above polymers (all methyl), reactive polymers can also be prepared. This can be achieved when re-equilibrating oligomers or existing polymers:



to obtain a polydimethyl-methylhydrogenosiloxane, $\text{MD}_z\text{D}^{\text{H}}_w\text{M}$. This polymer can be further functionalised using an addition reaction:



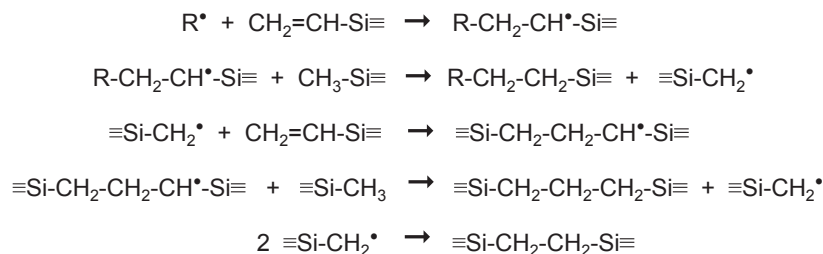
The above polymers are all linear apart from the cyclics, but these are also made up of difunctional units, D. Apart from these, branched polymers or resins can be prepared if, during hydrolysis, a certain amount of T or Q units are included, which will allow an expansion of the material, not in two, but in three or four directions. This can be described if considering the hydrolysis of the methyltrichlorosilane in the presence of trimethylchlorosilane, which leads to:



or $(\text{Me}_3\text{SiO}_{1/2})_x (\text{MeSiO}_{3/2})_y$ or M_xT_y . The formation by hydrolysis of three silanols on the MeSiCl_3 no longer gives through condensation a linear polymer but now a three-dimensional structure or resin. The average molecular weight depends upon the amount of M units that come from the trimethylchlorosilane, which limits the growth of the resin molecule. Most these resins are prepared in a solvent and usually contain some residual hydroxyl groups. These could subsequently be used to cross-link the resin and form a continuous network or varnish.

Silicone elastomers. Silicone polymers are easily transformed into a three-dimensional network and an elastomer via a cross-linking reaction, which allows the formation of chemical bonds between adjacent chains. This is achieved according to one of the following reactions.

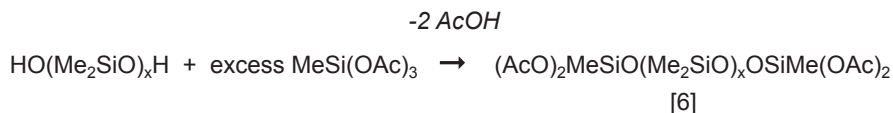
Cross-linking with radicals. Efficient cross-linking with radicals is only achieved when some vinyl groups are present on the polymer chains. The following mechanism has been proposed for the cross-linking made by radicals generated from an organic peroxide:⁵



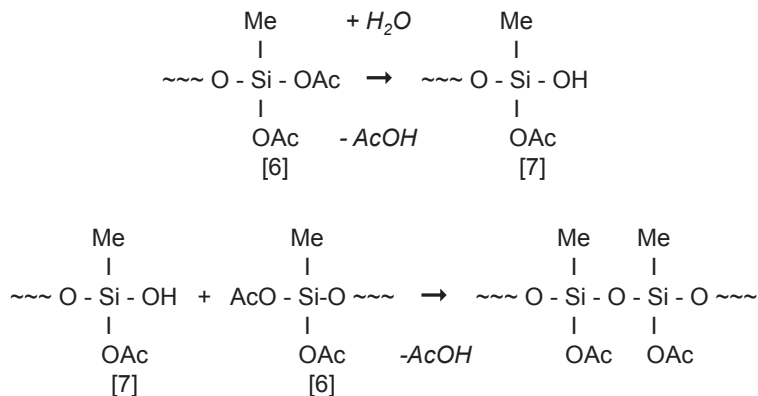
where \equiv represents two methyl groups and the rest of the polymer chain.

This reaction is used for high-consistency silicone rubbers (HCRs) such as those used in extrusion or injection moulding and which are cross-linked at elevated temperatures. The peroxide is added before use. During cure, some precautions are needed to avoid the formation of voids by the volatile residues of the peroxide. Post cure may also be necessary to remove these volatiles, which can act as depolymerisation catalysts at high temperatures.

Cross-linking by condensation. This method is used in sealants such as the ones available from “do-it-yourself” shops. These products are ready to use and require no mixing. Cross-linking starts when the product is squeezed from the cartridge and comes into contact with moisture. They are formulated from a reactive polymer prepared from a hydroxy-endblocked polydimethylsiloxane and a large excess of methyltriacetoxysilane:

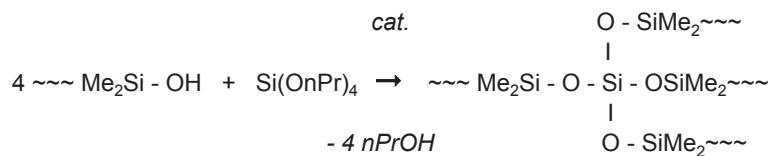


As a large excess of silane is used, the probability of two different chains reacting with the same silane molecule is remote and all the chains are endblocked with two -OAc functions. The resulting product is still liquid and can be stored in sealed cartridges. Upon opening and contact with the moisture of the air, the acetoxy groups are hydrolysed to give silanols, which allow further condensation to occur:



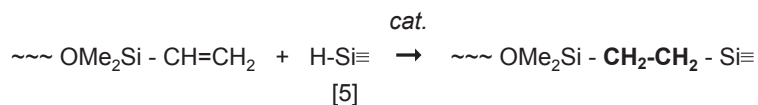
In this way, two chains have been linked, and the reaction proceeds further from the remaining acetoxy groups. An organometallic tin catalyst is normally used. This cross-linking requires that moisture diffuses within the product and the cure proceeds from the outside surface, towards the inside. These sealants are called one-part sealant RTV (room temperature vulcanisation) but actually require moisture as a second component. Acetic acid is released as a byproduct of the reaction, and corrosion problems are possible on substrates such as concrete, with the formation of a water-soluble salt at the interface (and loss of adhesion at the first rain!). To overcome this, other systems have been developed. These include one-part sealants releasing less corrosive or noncorrosive byproducts; for example, oxime using the oximosilane $\text{RSi}(\text{ON}=\text{CR}'_2)_3$ or alcohol using the alkoxysilane $\text{RSi}(\text{OR}')_3$ instead of the above acetoxysilane.

Condensation curing is also used in two-part systems where cross-linking starts upon mixing the two components; for example, a hydroxy-endblocked polymer and an alkoxysilane such as tetra n-propoxysilane:



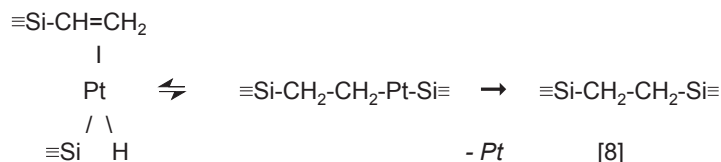
Here, no atmospheric moisture is needed; usually an organotin salt is used as catalyst but it also limits the stability of the resulting elastomer at high temperatures. Alcohol is released as a byproduct of the cure, leading to slight shrinkage upon cure. This precludes the fabrication of very precise objects (0.5 to 1% linear shrinkage).

Cross-linking by addition. The above shrinkage problem can be eliminated when using an addition reaction to achieve cross-linking. Here, cross-linking is achieved using vinyl-endblocked polymers and reacting them with SiH groups carried by a functional oligomers such as described above [5]. A few polymers can be bonded to this functional oligomer [5], as follows:⁵



where \equiv represents the remaining valences of the Si in [5].

The addition occurs mainly on the terminal carbon and is catalysed by Pt or Rh metal complexes, preferably organometallic compounds to enhance their compatibility. The following mechanism has been proposed (oxidative addition of the $\equiv\text{SiH}$ on the Pt, H transfer on the double bond and reductive elimination of the product):



where to simplify, other Pt ligands and other Si substituents are omitted.

There is no byproduct with this reaction, and moulded pieces made with a product using this cure mechanism are very accurate (no shrinkage). However, handling these two-part products (i.e., polymer and Pt catalyst in one component, SiH oligomer in the other) requires some precautions. The Pt in the complex is easily bonded to electron-donating substances like amine or organosulphur compounds to form stable complexes with these poisons, rendering the catalyst inactive (inhibition).

Physicochemical Properties

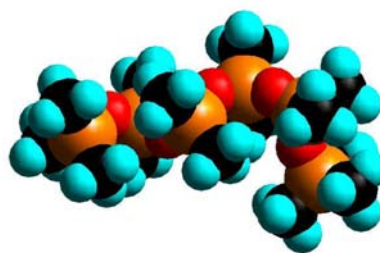
The position of silicon, just under carbon in the periodic table, led to a belief in the existence of analogue compounds where silicon would replace carbon. Most of these analogue compounds do not exist or behave very differently. There are few similarities between Si-X bonds in silicones and C-X bonds:^{3,5}

Element (X)	Bond length (Å)		Ionic character (%)	
	Si-X	C-X	Si-X	C-X
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 Si, bond lengths are longer than for C with this element. The lower Si electronegativity (1.8) vs. C (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 (see above). Si 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 allow $d\pi\text{-}p\pi$ retro-coordination. Because of this retro-coordination, trialkylsilanols are more acid than the corresponding alcohols. Yet, the involvement of retro-coordination is challenged.⁸ Another example of the difference between analogues is the tetravalent diphenyldisilanol, $(\text{C}_6\text{H}_5)_2\text{Si}(\text{OH})_2$, which is stable, while its carbon equivalent, a gem-diol, will dehydrate. 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.⁸ The Si-O bonds are strongly polarised and without protection should lead to strong intermolecular interactions.⁵ However, the methyl groups, only weakly interacting with each other, shield the main chain (Figure 1).

Figure 1. Three-dimensional representation of tetradecamethylhexasiloxane,⁹ $\text{Me}_3\text{SiO}(\text{SiMe}_2\text{O})_4\text{SiMe}_3$ or MD_4M .



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 $\text{CH}_2\text{-CH}_2$ bond in polyethylene is 13.8 kJ/mol but only 3.3 kJ/mol around a $\text{Me}_2\text{Si-O}$ 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 a “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.⁸

The ease with which silicones adopt many conformations is confirmed by monolayer absorption studies on water. Two structures have been proposed, an open one where the Si-O-Si bonds are oriented towards the aqueous phase, and a more compact one where the chain adopts a helicoidal structure. The important point is the low energy difference between these two structures, demonstrating once again the flexibility of the siloxane chain.⁷

The surface activity of silicones is displayed in many circumstances:⁸

- 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 glycol copolymers).

The low intermolecular interactions in silicones have other consequences:⁸

- Glass transition temperatures are very low (e.g., 146 K for a polydimethylsiloxane compared to 200 K for polyisobutylene, the analogue hydrocarbon).
- 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 the silicone 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.⁵

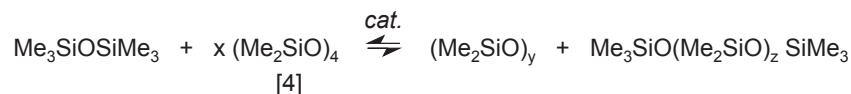
The presence of groups other than methyl along the chain leads to a reduction of the polymer’s thermal stability, but with this substitution, some of the above properties can be modified:

- A small percentage of phenyl groups along the chain perturbs sufficiently to affect 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/cm^3)^{1/2}. These copolymers are used to prepare elastomers with little swelling in alkane or aromatic solvents.

Silicone Analysis

Among the many analytical methods used for silicones,¹⁰ only a few are presented here.

Composition can easily be analysed by chromatography. This allows quantifying the low molecular weight oligomers present in silicone polymers. As mentioned above, (see *Polymerisation and polycondensation*), polymerisation reactions lead to the formation of two molecular weight distributions, cyclics around a degree of polymerisation y and polymers around a degree of polymerisation z :



Various techniques can be used to evaluate the polymers and to identify and quantify the lowest molecular weight species present: GC, GPC or SFC (Figure 2).

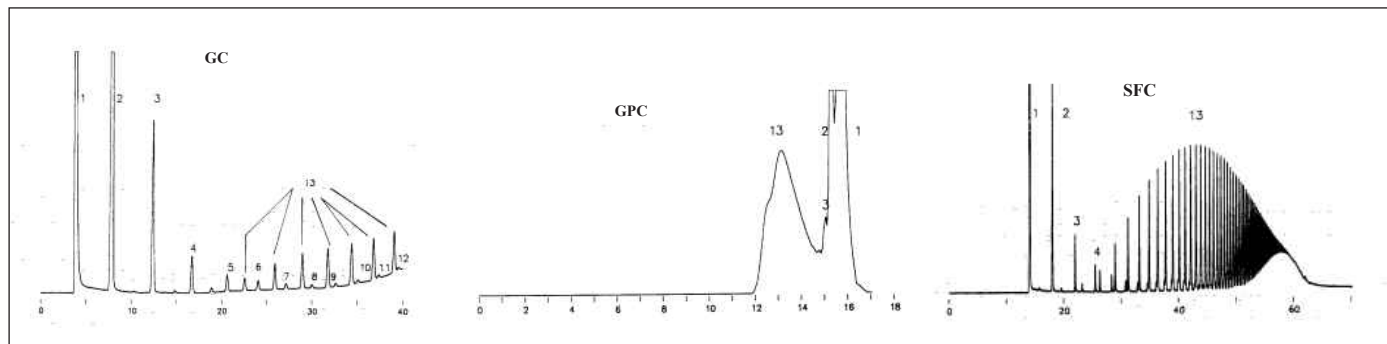
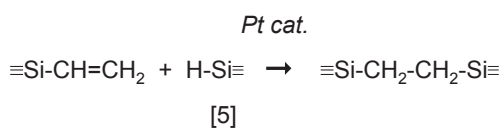


Figure 2. Comparison between different chromatographic techniques with a trimethylsilyloxy terminated polydimethylsiloxane before stripping.¹¹ Peak 1 to 12 = cyclics ($y = 4$ to 15) and peak 13 = polymer. Reproduced by permission of John Wiley Sons, Inc. from the *Analytical Chemistry of Silicones*, A. Lee Smith edit., copyright © 1991 John Wiley and Sons, Inc.

Structure can be analysed by NMR of the ^{29}Si ($I=1/2$) because of its high relative abundance (4.7 %). The interpretation is eased by large chemical shifts. This allows identifying and studying the distribution of various groups within a copolymer (Figure 3).

Digital scanning calorimetry can be used to study the addition reaction used to cross-link silicone elastomers:



which is characterised by an exotherm ($-\Delta H = 120 - 170$ kJ/mol). This allows characterisation of the cross-linking and optimisation of the elastomer formulation based on the temperatures corresponding to the onset of cure or the maximum cure rate (Figure 4).

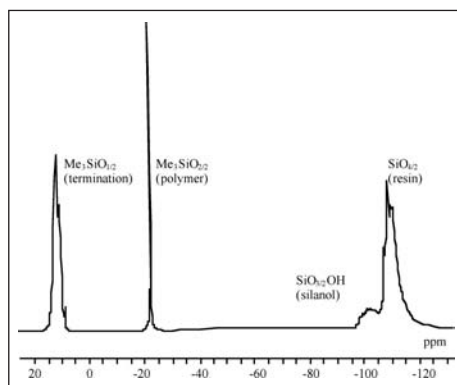


Figure 3. ^{29}Si NMR spectrum of a silicone pressure sensitive adhesive (PSA).¹²

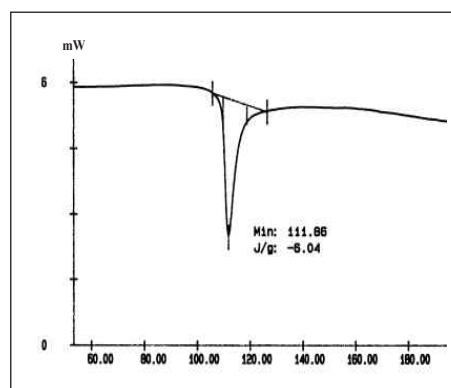


Figure 4. Differential scanning calorimetry of the reaction between polymers with SiVi groups and with SiH groups in presence of a Pt catalyst.¹³

Toxicology

The most widely used silicones are the polydimethylsiloxanes, $\text{Me}_3\text{SiO}(\text{SiMe}_2\text{O})_n\text{SiMe}_3$, with viscosities between 10 to 100,000 mPa.s. These have not shown toxicity during administration via typical exposure routes. Due to their high molecular weight, they are not absorbed in the gastrointestinal tract and are excreted without modification, nor are they absorbed through the skin.¹⁴ *In vitro* studies have not indicated mutagenic effects.¹⁴ Repeated oral or cutaneous dosages have not indicated effects on different species.¹⁴ Inhalation of aerosols of oily or fatty-type materials, including silicones, into alveolar regions of the lung may result in physical disturbances of the lining of the lung with associated effects.¹⁵

Lower molecular weight siloxanes are frequently used due to their volatility and generally dry skin feel. These can include linear as well as cyclic siloxanes.

The lowest molecular weight linear material is hexamethyldisiloxane, $\text{Me}_3\text{SiOSiMe}_3$ (HMDS), which has a viscosity of 0.48 mPa.s. HMDS has generally shown few effects toxicologically, though recent data have indicated slightly earlier incidence of testicular tumors in male rats exposed to high levels of material via inhalation; the relevance of this effect to humans is not yet known.¹⁶ Other linear molecules of three, four, or five siloxane units do not exhibit toxic effects, though the data are limited for long-term exposure.¹⁷ The materials have very limited absorption via typical exposure routes. Like the higher molecular weight polymers, the low molecular weight linears are not mutagenic, irritating or acutely toxic.

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. None of these materials has exhibited toxicity except for the four member cyclic (n=4), which has shown a reduction in litter size with a reduction of implantation sites in the uterus of exposed female rats. This effect is not expected to occur in humans.^{18,19} These effects were not measured in the five (n=5) member or other cyclic siloxanes.²⁰

Epidemiology

With the resolution of the legal controversy regarding silicone gel-filled breast implants well underway, these medical devices remain available with some restriction in the U.S., where they have been used since the early 1960s. Outside of the U.S. and Canada, however, access to these devices is unconstrained. The controversy in the 1990s initially involved breast cancer, then evolved to autoimmune connective tissue disease, and continued to evolve to the frequency of local or surgical complications such as rupture, infection or capsular contracture. Epidemiology studies have consistently found no association between breast implants and breast cancer.²¹⁻²⁷ In fact, some studies suggest that women with implants may have decreased risk of breast cancer.^{25,26} Reports of cancer at sites other than breast are inconsistent or attributed to lifestyle factors.²⁸ The research on autoimmune or connective tissue disease has also been remarkably uniform and concludes there is no causal association between breast implants and connective tissue disease.²⁹⁻³⁴

Impact on the Environment

A large number of studies have been conducted to evaluate the fate and effects of silicones in the environment throughout their life cycle.¹⁴ Manufacture of polydimethylsiloxanes is strictly controlled and emissions to the environment from this phase are very small. Subsequently, the environmental fate of silicones depends to a large extent on the physical form of the material and the method of disposal. Polydimethylsiloxanes are used as ingredients in numerous consumer products (e.g., in personal care or household care products) or in many industrial processes (e.g., demoulding agents or lubricants).

“Solid” silicones (e.g., silicone elastomers or sealants) enter the environment as a component of domestic or municipal waste and must be either landfilled or incinerated. In the latter case, they are converted back to inorganic ingredients, amorphous silica, carbon dioxide and water vapour. “Liquid” silicones, 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 silicones used as antifoamers in pharmaceuticals. Because most silicones are virtually insoluble in water, combined with 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 streams borders the level of detection (5 µg/l).^{35,36}

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 sludge-bound polydimethylsiloxanes to soil caused no observed adverse effects on crop growth or soil organisms.³⁷ Little or no uptake into the plants was observed, which is consistent with animal studies showing that high molecular weight polydimethylsiloxanes are too large to pass through biological membranes of either plants or animals. Extensive studies ranging from small scale laboratory tests^{38,39} to field studies^{37,40} show that sewage-sludge bound polydimethylsiloxanes degrade in soils as a result of contact with clay minerals. The clay acts as a catalyst to depolymerise the siloxane backbone.³⁸ The primary degradation product, regardless of the polydimethylsiloxane molecular weight, is dimethyldisilanol, $\text{Me}_2\text{Si}(\text{OH})_2$.³⁹ Depending on the soil type, this undergoes further degradation either in the soil via biodegradation⁴¹ or evaporates into the atmosphere,⁴² where it degrades oxidatively via reaction with hydroxyl radicals.⁴³ Whether degradation occurs in the soil or in the air, there is conversion to inorganic constituents, amorphous silica, carbon dioxide and water.

Low molecular weight silicones (e.g., the linear or cyclic siloxanes used in personal care applications) display a different environmental profile. As a consequence of their very high volatility, they readily evaporate into the air, where they degrade as a result of reaction with hydroxyl radicals in the presence of sunlight. Based on their chemical structure, they are not predicted to cause ozone depletion or contribute significantly to global warming.⁴⁴ Studies have shown that they do not cause ozone formation in the lower atmosphere, and as a consequence these volatile siloxanes have been granted an exemption from the volatile organic compounds (VOC) regulations by the EPA in the U.S.

These materials are not biodegradable. As a consequence of this and the fact that they have the potential to bioaccumulate in a sealed system, the Oslo Paris Commission (OSPAR), which is concerned with the discharge of man-made substances into the marine environment, has identified hexamethyldisiloxane (HMDS) as a potential “Priority Hazardous Substance.” The European Silicone Industry Association (CES) is therefore conducting a risk assessment on HMDS using the EU model (EUSES). However, as both modelling data and environmental monitoring do not indicate any significant inputs into the marine environment, the European Silicone Industry is confident of a favourable outcome from the risk assessment.

Performance and Applications

Thermal aging resistance. Silicones are used in numerous applications requiring high temperature resistance.^{5,7} During thermogravimetry and in absence of impurities, polydimethylsiloxane degradation starts only at around 400°C. Yet the term “thermal stability” must be used with caution, as its meaning is largely dependent on the application considered and often implies many different properties such as depolymerisation, oxidation or fire resistance. Applications are diffusion pump fluids, heat transfer fluids, elastomers for oven seals or for electrical cable insulation. In case of fire, a silicone elastomer insulating an electrical cable decomposes to give insulating silica rather than electrically conducting carbon as produced by the combustion of an hydrocarbon elastomer.

Chemical aging and weathering resistance. Silicones can be degraded, particularly at elevated temperatures, by substances capable of acting as depolymerisation catalysts.⁵ However, the hydrophobic nature of silicones limits the extent of their contact with many aqueous solutions and allows their use in the presence of many chemical compounds. Swelling of elastomers in common solvents can be reduced by using copolymers (see above).

Silicones are used in the building industry as sealants. Their success is linked to their outstanding weathering resistance: low reactivity of the various bonds towards polluted air or water, hydrophobicity that limits any water contact and UV transparency explain the performance. Other properties make silicones suitable as building sealants. They are easy to pigment as they are transparent at visible wavelengths, and the low chain-to-chain interaction results in elastomers with very low modulus, which reduces permanent joint stresses and increases longevity.

Release properties. Transfer paper for self-adhesive labels is fabricated with silicone paper coatings.⁸ Silicones are applied as liquid before curing them, usually via an addition reaction (see above) to give film-coated paper. Self-adhesive labels can be applied to this paper without risk of permanent bonding. The adhesive surface tension (30 to 40 mN/m) does not allow enough wetting of the silicone, and this reduces the actual contact surface and the adhesion work to allow easy removal of the label from the silicone-coated paper.

Similarly, a silicone elastomer can be used to prepare a mould from an original object like a sculpture, which is covered with a two-part elastomer (see above). The low surface tension of the silicone allows perfect wetting of the original surface and gives, after cure, a perfect negative. Plaster or a thermosetting resin can be cast in this mould to give a copy that has all the details of the original master. The low surface energy of the silicone allows easy demoulding of this copy.

Biocompatibility. The innocuity of silicones explains their numerous applications where prolonged contact with the human body is involved: on textile fabrics, in cosmetics, in contact with foods and in medical applications. Silicone elastomers are used in many medical devices, like Class II or III medical devices regulated by the European Medical Devices Directive, such as tubing for extracorporeal circulation used during cardiac surgery, hydrocephalic shunts or pacemaker leads. Their excellent biocompatibility is partly due to the low chemical reactivity displayed by silicones, their low surface energy and their hydrophobicity.⁸

Conclusions

Polydimethylsiloxanes are formed from compounds that are largely available: sand and methanol, and if necessary, the latter can be produced from wood distillation.⁸ Often referred to as silicones, they are used in many applications because of their stability, low surface tension and lack of toxicity. Methyl group substitution or introduction of tri- or tetra-functional siloxane units leads to a wide range of structures. Polymers are easily cross-linked at room or elevated temperature to elastomers, without losing the above properties. These factors explain the commercial success of silicones and should support their future development.

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