Chapter 53

Silicones

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Since silicone lies beneath carbon in the periodic table, one might assume that silicone chemistry closely approximates that of the carbon analogs. In actuality, silicone chemistry much more closely resembles that of boron than carbon.

Physical-Chemical Properties

Silicon is larger and less electronegative than carbon; thus the resulting bonds to oxygen and chlorine are more electronegative. Silicon does form tetrahedral bonds as does carbon, but unlike carbon, silicon has d-orbitals available for bonding. The S–O bond angle and bond distance are both larger than the C–C and C–O bonds. Additionally, silanols, unlike the very stable alcohols, will typically undergo spontaneous hydrolysis to form siloxanes. In general, silicon compounds are much more reactive than their carbon analogues.

Low-molecular-weight silicone fluids are also more volatile than their organic counterparts. This volatility approaches a limit with fluids of approximately 10 cSt or higher.

As with volatility characteristics, other properties of dimethicone fluids also change with increasing molecular weight or degree of polymerization. For example, low-viscosity fluids are soluble in mineral oil and solvent alcohols such as ethanol or isopropanol, while the fluids most commonly employed in personal care applications (100 cSt and higher) are not. Table 1 lists solubility characteristics of three silicone fluids commonly employed in personal care applications.

As compared to their organic counterparts, dimethylsiloxane polymers display much greater thermal and oxidative stability, and are fluid

Table 1. Solubility Characteristics of Selected Silicones

Material	100 cst Dimethicone	Cyclomethicone	Phenyltrimethicone
Ethanol	NS	S	S
Isopropanol	NS	S	S
Water	NS	NS	NS
Isopropyl palmitate	S	S	S
Isopropyl myristate	S	S	S
Mineral oil	NS	S	S
Beeswax	NS	SH	SH
Carnauba wax	NS	SH	SH
Aromatic solvents	S	S	S
Aliphatic solvents	S	S	S
Octylmethoxycinnamate	PS	S	S
Octyl salicylate	NS	S	S
Lanolin	NS	SH	SH

*S = Soluble, NS = Not Soluble, PS = Partially Soluble, SH = Soluble Hot

over a much larger range of molecular weights. Polydimethylsiloxanes undergo a very small change in physical properties with either temperature or polymer molecular weight, which accounts for their low modulus and glass transition temperatures, and the high vapor permeability exhibited by dimethicone fluids. These differences between silicone and organic polymers result from the weak intermolecular attractive forces characteristic of silicone polymers—a consequence of a combination of factors:

- Large Si–O bond angles
- Greater degree of rotation about the Si–O bond as compared to carbon-based compounds
- Freely rotating methyl groups, which swing to the surface and tend to keep the polymer chains more extended, resulting in a large excluded or "free" volume

Also characteristic of polydimethylsiloxanes is a low surface tension (20.8 N/m^2 at 25^{o}C), coupled with high spreadability and diffusivity

Table 2. Gas Permeability of a Silicone Elastomer as Compared to Organic Polymers

Compound	**Gas Permeability (106 cm^3/s/cm)**
Silicone rubber	60
Natural rubber	2.4
Butyl rubber	0.24
Polyvinyl chloride	0.014
Teflon	0.0004

coefficients. Therefore, the unmodified silicone polymers will spread into thin uniform films and are highly permeable to gases such as oxygen, carbon dioxide and water vapor. This is illustrated in Table 2, where the gas permeability of silicone elastomers is compared to several other organic compounds.

However, replacement of one or more of the methyl groups in polydimethylsiloxanes by larger aliphatic or aromatic hydrocarbon substituents markedly decreases both the spreading capacity of the fluids and the permeability of the resulting polymers. (Noll 1968) These characteristic properties are responsible for the unique attributes of silicone polymers, which render them useful in a large variety of applications in such diverse industries as aerospace, electronics, automotive, construction and cosmetics.

Silicone Chemistry

There are several different processes utilized on a commercial scale in order to manufacture silicones. Each production process contains numerous steps, starting with the preparation of silicon metal, followed by formation of chlorosilanes and their subsequent conversion first to silanols and then ultimately to organosiloxanes. The most widely utilized commercial process, referred to as the "direct process" or the Rochow synthesis, is illustrated in Figure 1.

The first step in the illustrated process is known as a carbothermic reduction, where sand is mixed with coke in an electric furnace to produce

Figure 1. Preparation of Monomeric Siloxane Units

1) Carbothermic Reduction:

$$\underset{\text{(sand)}}{SiO_2} \; + \; \underset{\text{(coke)}}{2C} \; \xrightarrow[\text{Furnace}]{\text{Electric}} \; 2CO_2 \; + \; Si\ \text{(metal)}$$

2) Direct Process:

$$Si + CH_3Cl \xrightarrow[300^{\circ}C]{Cu} \text{Mixture of Chlorosilanes}$$

Trimethylchlorosilane	Me_3SiCl
Dimethyldichlorosilane	Me_2SiCl_2
Methyltrichlorosilane	$MeSiCl_3$
Tetrachlorosilane	$SiCl_4$

Chlorosilanes are separated by distillation, process is optimized to yield Me_2SiCl_2

3) Hydrolysis:

$$\begin{aligned}
Me_3SiCl + H_2O &\longrightarrow Me_3SiOH &&\longrightarrow Me_3SiO_{1/2} + H_2O\\
Me_2SiCl_2 + H_2O &\longrightarrow Me_2Si(OH)_2 &&\longrightarrow Me_2SiO_{2/2} + H_2O\\
MeSiCl_3 + H_2O &\longrightarrow MeSi(OH)_3 &&\longrightarrow MeSiO_{3/2} + H_2O\\
SiCl_4 + H_2O &\longrightarrow Si(OH)_4 &&\longrightarrow SiO_{4/2} + H_2O
\end{aligned}$$

4) Cracking / Distillation:

Siloxanes -----> Trimer + Tetramer + Pentamer + Hexamer + etc.

5) The Equilibrium Reaction:

$$(CH_3)_3Si\text{-}O\text{-}Si(CH_3)_3 + x\,[(CH_3)_2Si\text{-}O]_4 \;\underset{\Delta}{\overset{\text{Catalyst}}{\longleftrightarrow}}\; \underset{(MD_{4x}M)}{(CH_3)_3Si\text{-}O\text{-}[(CH_3)_2SiO]_{4x}\text{-}Si(CH_3)_3}$$

At equilibrium 12-15% volatiles remain

silicon metal. Next, the metal is crushed to a particle size range of 45-250 mm and mixed with copper powder. The silicon-copper mixture is placed onto a septum in a large vertical steel cylinder known as a fluid-bed reactor. Then, a heated stream of methyl chloride gas is passed through the mixture, forcing the powder upward in the column. The temperature of this reaction must be strictly controlled, and is typically kept in the range of 280-290°C. (Rochow 1987) This reaction may be accelerated by addition of up to 0.2% zinc dust. (Tomanek 1991)

The resulting reaction products are a mixture of chlorosilanes with varying degrees of substitution. The chlorosilanes formed during this reaction are separated by subsequent distillation columns (to a purity of ~99.98 mole %) in the order of increasing boiling points. The production process is optimized to yield dimethyldichlorosilane, which is the most important product for the synthesis of silicone polymers.

The next step in the Rochow process is known as a hydrolysis reaction, in which the various silanol groups are formed. The silanols undergo spontaneous condensation to form low-molecular-weight siloxanes, or hydrolysates. The monomeric and oligomeric hydrolysates may be used in the production of silicone polymers via polycondensation reactions, or may be "cracked back" to generate a series of cyclic siloxanes. Both intramolecular and intermolecular condensation can occur, with the former yielding ring structures and the latter, linear polymers. (Tomanek 1991) Polymethylsiloxanes may be formed by reaction of hydrolysate as described above using a phosphorous nitrile chloride ($PNCl_2$) catalyst, or by ring opening polymerization of cyclic siloxanes in an equilibrium or redistribution reaction as shown in Figure 1. (Tyler 1954; Rochow 1940; Sprung 1946; McGregor and Warrick 1942; Marsden and G.F. Rodel 1945; Spier 1952; Tyler 1950; Agnes 1944)

Silicone Nomenclature

The system of nomenclature employed for silicone chemistry is very similar to that used to name organic compounds. In 1904, Frederick Kipping coined the term silicone for the basic monomeric unit—$(CH_3)_2SiO$—because he thought it was similar to an organic ketone structure. It was later learned that this compound does not exist as such because silicon does not form a double bond to oxygen as does carbon, but rather one oxygen atom is shared between two silicon atoms as in hexamethyl disiloxane, $(CH_3)_3Si\text{-}O\text{-}Si(CH_3)_3$.