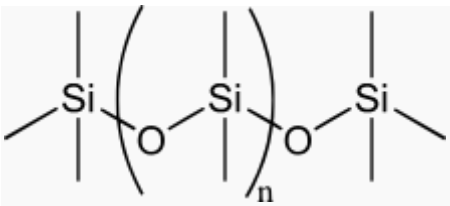
Lecture #10: The polymeric silicon compound.

Silicones are polymers that include any inert, synthetic compound made up of repeating units of siloxane, which is a chain of alternating silicon atoms and oxygenatoms, frequently combined with carbon and/or hydrogen. They are typically heat-resistant and rubber-like, and are used in sealants, adhesives, lubricants, medicine, cooking utensils, and thermal and electrical insulation. Some common forms includesilicone oil, silicone grease, silicone rubber, silicone resin, and silicone caulk

Chemistry



Chemical structure of the silicone polydimethylsiloxane (PDMS).

More precisely called polymerized siloxanes or polysiloxanes, silicones consist of an inorganic silicon-oxygen backbone chain (···-Si-O-Si-O-Si-O-···) with organic side groups attached to the silicon atoms. These silicon atoms are tetravalent. So, silicones are polymers constructed from inorganic-organic monomers. Silicones have in general the chemical formula $[R_2SiO]_n$, where R is an organic group such asmethyl, ethyl, or phenyl.

In some cases, organic side groups can be used to link two or more of these -Si-O- backbones together. By varying the -Si-O- chain lengths, side groups, andcrosslinking, silicones can be synthesized with a wide variety of properties and compositions. They can vary in consistency from liquid to gel to rubber to hard plastic. The most common siloxane is linear polydimethylsiloxane (PDMS), a silicone oil. The second largest group of silicone materials is based on silicone resins, which are formed by branched and cage-like oligosiloxanes.

Terminology and history

F. S. Kipping and Matt Saunders coined the word *silicone* in 1901 to describe polydiphenylsiloxane by analogy of its formula, Ph_2SiO (Ph stands for phenyl, C_6H_5), with the formula of the ketone benzophenone, Ph_2CO (his term was originally*silicoketone*). Kipping was well aware that polydiphenylsiloxane is polymeric whereas benzophenone is monomeric and noted that Ph_2SiO and Ph_2CO had very different chemistry.[2][3] The discovery of the structural differences between Kippings' molecules and the ketones means that *silicone* is no longer the

correct term (though it remains in common usage) and that the term *siloxanes* is correct according to the nomenclature of modern chemistry.[4]

Silicone is sometimes mistakenly referred to as silicon. The chemical element silicon is a crystalline metalloid widely used in computers and other electronic equipment. Although silicones contain silicon atoms, they also include carbon, hydrogen, oxygen, and perhaps other kinds of atoms as well, and have very different physical and chemical properties to elemental silicon.

A true *silicone group* with a double bond between oxygen and silicon does not commonly exist in nature; chemists find that the silicon atom usually forms single bonds with each of two oxygen atoms, rather than a double bond to a single atom. Polysiloxanes are among the many substances commonly known as "silicones".

Molecules containing silicon-oxygen double bonds do exist and are called silanones but they are very reactive. Despite this, silanones are important as intermediates in gas-phase processes such as chemical vapor deposition in microelectronicsproduction, and in the formation of ceramics by combustion.[5]

Synthesis

Silicon dioxide (silica), used in the manufacture of all silicones.

This section requires expansionwith: functional group types. *(April 2015)*

Most common are materials based on polydimethylsiloxane, which is derived by hydrolysis of dimethyldichlorosilane. This dichloride reacts with water as follows:

$$n\ Si(CH_3)_2Cl_2 + n\ H_2O \rightarrow [Si(CH_3)_2O]_n + 2n\ HCl$$

The polymerization typically produces linear chains capped with Si-Cl or Si-OH (silanol) groups. Under different conditions the polymer is a cyclic, not a chain.[1]

For consumer applications such as caulks silyl acetates are used instead of silyl chlorides.[*clarification needed*] The hydrolysis of the acetates produce the less dangerous acetic acid (the acid found in vinegar) as the reaction product of a much slower curing process. This chemistry is used in many consumer applications, such as silicone caulk and adhesives.

Branches or cross-links in the polymer chain can be introduced by using organosilicon precursors with fewer methyl groups, such as methyltrichlorosilane and methyltrimethoxysilane. Ideally, each molecule of such a compound becomes a branch point. This process can be used to produce hard silicone resins. Similarly, precursors with three methyl groups can be used to limit molecular weight, since each such molecule has only one reactive site and so forms the end of a siloxane chain.

Combustion

When silicone is burned in air or oxygen, it forms solid silica (silicon dioxide) as a white powder, char, and various gases. The readily dispersed powder is sometimes called silica fume.

Properties

Silicones exhibit many useful characteristics, including:[1]

- Low thermal conductivity
- Low chemical reactivity
- Low toxicity
- Thermal stability (constancy of properties over a wide temperature range of −100 to 250 °C).
- The ability to repel water and form watertight seals.
- Does not stick to many substrates, but adheres very well to others, e.g. glass.
- Does not support microbiological growth.
- Resistance to oxygen, ozone, and ultraviolet (UV) light. This property has led to widespread use of silicones in the construction industry (e.g. coatings, fire protection, glazing seals) and the automotive industry (external gaskets, external trim).
- Electrical insulation properties. Because silicone can be formulated to be electrically insulative or conductive, it is suitable for a wide range of electrical applications.

- High gas permeability: at room temperature (25 °C), the permeability of silicone rubber for such gases as oxygen is approximately 400 times[*citation needed*] that of butyl rubber, making silicone useful for medical applications in which increased aeration is desired. Consequently, silicone rubbers cannot be used where gas-tight seals are necessary.

Uses

Silicones are used in many products. Ullmann's Encyclopedia of Industrial Chemistry lists the following major categories of application: Electrical (e.g., insulation), electronics (e.g., coatings), household (e.g., sealants for cooking apparatus), automobile (e.g., gaskets), aeroplane (e.g., seals), office machines (e.g., keyboard pads), medicine/dentistry (e.g., teeth impression molds), textiles/paper (e.g., coatings). For these applications, an estimated 400,000 tons of silicones were produced in 1991.

Reference:

https://en.wikipedia.org/wiki/Silicone