Silicone Polymers: History & Chemistry

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INTRODUCTION

Silicones are a general category of synthetic polymers whose backbone is made of repeating silicone to oxygen bonds (siloxane bonds) with organic side groups, such as methyl, phenyl or vinyl. The number of repeating units can range from one to several thousand.

The word siloxane is derived from the words Silicone, Oxygen and Alkane. This is the basis for the name silicones, which was assigned by Kipping based on their similarity with ketones, because in most cases there is on average one silicone atom for one oxygen and two methyl groups (Kipping, 1904). The basic repeating unit became known as siloxane and the most common available silicone is polydimethylsiloxane (PDMS).

Polysiloxanes are among the most versatile specialty molecule known to man. As of now over 7,000 specialty products are based on polysiloxane. Some 85% of silicone applications are surface related, specifically for surface modifications. They would include lubrication and release applications. They could be found in products such as cosmetics, food additives, deodorant and soap. They are inert and stable under wide pH range. They are increasingly been seen as alternate to perchloroethylene, which is widely considered environmentally undesirable for dry cleaning.

Polymerized siloxanes with organic side chains are commonly known as Polysiloxane. Representative examples are dimethyl siloxane $[SiO(CH_3)_2]_n$ and diphenyl siloxane $[SiO(C_6H_5)_2]_n$. These compounds can be viewed as a hybrid of both organic and inorganic compounds. The organic side chains confer hydrophobic properties, while the –Si-O-Si-O- backbone is purely inorganic and offer high degree of flexibility to the molecule, their by imparting liquid state over a broad temperature range and high compressibility. Additionally, dimethyl groups offer low surface energy and hence low surface tension and high speadability. This gives silicones a combination of unique properties, making possible their use as fluids, resins, elastomers, emulsions, biomaterials in numerous applications and diverse fields.

Silicones are common in aerospace industry because of their low and high temperature performance. In the electronics field, silicones are used as electrical insulation, potting compounds and other applications specific to semiconductor manufacture. Their long term durability has made silicone sealants, adhesives and water proof coatings commonplace in the construction engineering. Their excellent biocompatibility makes many silicones well suited for use in various personal care, pharmaceutical and medical device applications.

Normally silicones are not compatible with organic polymers, but if a larger organic group is attached to a silicone, its properties are altered and it can be blended with organic polymers. This approach offers a unique method to combine unique properties of silicone with traditional organic molecules. Incorporation of organic groups into silicone backbone is accomplished through a reaction step known as hydrosilation. Needless to say, hydrosilation is the most fundamental reaction that has expanded application of silicones to wider field of applications. Hydrosilation is a chemical step, where an allyl group is attached, through an addition reaction to SiH group on the siloxane back bone, using platinum as catalyst. By blending the chemistry of silicone with chemistry of carbon, it is possible to create polymers with unique properties and superior performance characteristics.

In 1824, Berzelius discovers silicone by the reduction of potassium fluorosilicate with potassium:
$4K + K_2SiF_6 \longrightarrow Si + 6KF$.

Reacting silicone with chlorine gives a volatile compound later identified as tetrachlorosilane:
$SiCl_4 : Si + 2Cl_2 \longrightarrow SiCl_4$.

In 1863, Friedel and Craft synthesize the first silicone organic compound, tetraethylsilane:
$2Zn(C_2H_5)_2 + SiCl_4 \longrightarrow Si(C_2H_5)_4 + 2\,ZnCl_2$.

In 1871, Ladenburg observes that diethyldiethoxysilane in the presence of a diluted acid gives an oil that decomposes only at a very high temperature.

From 1901 to 1930, Kipping laid the foundation of organosilicone chemistry with the preparation of various silanes by means of Grignard reactions and the hydrolysis of chlorosilanes to yield large molecules.

In the 1940s , silicones becomes commercial materials after Dow Corning demonstrated the thermal stability and high electrical resistance of silicone resins and General Electric found a direct method (Racow process) to prepare silicones from silicon and methyl chloride using copper catalyst.

Special characteristics

Silicones are the only organic/inorganic hybrid polymers that have been extensively commercialized. This is true for several important reasons. The organic portion in polydimethylsiloxane is the methyl group. The surface energy of any substance is a direct manifestation of the intermolecular forces between molecules and in the case of methyl group, these forces are almost the weakest possible among hydrocarbon molecules; only aliphatic fluorocarbon groups are lower.

The inorganic siloxane backbone (- Si – O – Si -) is the most flexible polymer backbone, due to high degree of electrovalent bonding character of - Si – O- bond, available and this allows the methyl groups to be arranged and presented to their best effect. These effects are further enhanced by creation of helix structure of PDMS molecule with methyl groups facing outwards and oxygen facing inwards. This unique structure resembles nanosprings, having inert methyl groups exposed to environment. Hence PDMS provides one of the lowest energy surface known that can be bettered only by more expensive fluorocarbon polymers.

They also exhibit significantly higher solubility for oxygen as compared to water or many of the organic liquids. It is this unique surface behavior, coupled with molecular flexibility, imparted by Si – O – bond that accounts for many silicone applications such as adhesives, emulsions, antifoams and surfactants.

In many applications it is critical for the silicone product to stick to another material. Whether the silicone is used as a coating, sealant or adhesive, a low surface energy polymer is being stuck to another material and it is achieved by carefully designing and formulating silicone products that bond directly with the substrate.

Silicone polymers are widely used in water based processes and applications. Most silicone polymers are not water soluble. For aqueous delivery they are usually formulated as an emulsion - a dispersion of small droplets of silicone oil with in an aqueous surfactant solution. Silicone polymers formulated in this way are often used in cosmetics, industrial release or fabric care applications. The silicone usually brings functionality such as hair conditioning or mold release.

Silicones are uniquely man made materials; no cause of naturally occurring organosilicone compounds has ever been convincingly demonstrated, although inorganic silicon is an essential element for bone development. The properties of silicones are also unique and it is these unusual properties that account for the place of these materials in today's technology.

Compared with conventional organic polymers, many silicones show superior thermal properties. Some silicone elastomers remain flexible at -100^{0}C and retain their properties for long periods at 200^{0}C. Most of the common silicone polymers are not wetted by liquid water, but are quite permeable to water vapor and to other gases. Their resistances to ultraviolet and other radiation means that they weather well - paints based on silicone resins have extremely long life.

Their electrical properties are excellent and they are frequently used for wire enamels, encapsulants and potting compounds for electrical components and electric motor insulation.

Degradation of silicone polymers in nature

Many consumer products containing silicone polymer (PDMS) are used in various applications which allows them to enter municipal wastewater treatment plants. Because PDMS is so insoluble in water, it partitions onto the sludge, causing no adverse effect on the treatment plant. The sludge is then destroyed by incineration, entombed in a landfill or spread out on agricultural fields as a fertilizer. This latter disposal technique allows PDMS to enter the soil environment.

In soil, the PDMS can hydrolyze to small, water soluble siloxanes with the ultimate product being the monomeric dimethylsilanediol (DMSD). This hydrolysis is probably abiotic because it can take months to years in wet oil, but only days as the soil dries. If the sludge is first composted, PDMS will remain intact with no effect on the composting process and will then degrade after the compost is mixed in with soil.

The hydrolysis product DMSD can microbially degrade to CO_2 and inorganic silicate already present in the soil. The overall reaction is:

$$Me_3SiO(SiMe_2O)nSiMe_3\ \text{(PDMS)} \longrightarrow Me_2Si(OH)_2\ \text{(DMSD)}$$

Followed by:

$$Me_2Si(OH)_2 \xrightarrow{\text{Light/ Microbes}} CO_2 + \text{Inorganic Silicate}$$

An apparent contradiction to the degradation of silicones in nature is that polymers are used for many outdoor applications because of their stability to high temperatures and their resistance to UV and O_3 exposure. This stability during the polymers intended use is a bulk phenomenon. However when PDMS is disposed down the drain and is eventually applied to the soil as a component of sludge, it becomes dispersed at low concentrations on soil minerals. This allows the PDMS to contact the catalyst needed to begin its polymerization, which eventually results in its complete conversion to natural components.

Effects of Silicones on human health & the environment

Only few siloxanes are described in the literature with regards to health effects, and it is therefore not possible to make broad conclusions and comparisons of the toxicity related to short chained linear and cyclic siloxanes based on the present evaluation.

Data are primarily found on the cyclic siloxanes D4 (octamethylcyclotetrasiloxane), D5 (decamethylcyclopentasiloxane) and the short linear HMDS (hexamethyldisiloxane). These three siloxanes have a relatively low order of acute toxicity by oral, dermal and inhalatory routes and do not require classification for this effect. They are not found to be irritating to skin or eyes and are also not found sensitizing by skin contact.

Applications of silicone polymers

Health care applications

- Moulded parts - drainage accessories, external feeding, laboratory tubing, respiratory masks, drug delivery devices etc.
- Dental impression materials
- Extrusion and tubing - blood handling equipments, urological applications etc.
- Breast implants
- Baby care nipples for baby bottles and comforters, breast pumps.
- Control of releases of gastrointestinal gases.
- Prostetics – linear & sockets

Cosmetics & Toiletries

- Hair care products mainly conditioning and hair styling products, but siloxanes may also be used in shampoos and colors.
- Skin care products such as body care, facial care and sun screen products.
- Shaving products such as pre-shave and after-shave lotion and shaving foam.
- Liquid soap and shower gels.
- Decorative and color cosmetic products, i.e. eye makeup, foundations, lipsticks and powders.
- Antiperspirants and deodorants mainly in stick deodorants but siloxanes may also be used in aerosols, creams, gels etc.

Sealants used for construction

- One component RTV silicones: mainly used in the construction industry for sealants around windows and doors, in bathrooms, expansion joints between dissimilar materials.
- Two-Components RTV silicones: mainly used for sealing of electronic components and sealed glazing units.
- Besides pure silicone sealants: a number of different hybrid sealants in which the Siloxanes are blended with other polymers like polyurethanes, acrylics and isobutylene exist.

Typical one component RTV silicone sealants consist of the following components (Krogh 1999) 60-80 % siloxane, 5-7% cross linking agent, 20-30% $CaCO_3$ filler, 1-6% silica filler, 5-20 % drying agents, and 0.05-0.10 % organotin catalyst.

Other applications

- Domestic applications like gasketing, electronics, sealing and potting.
- Consumer goods such as protective masks, baking tins, consumer products packing and soft touch products.
- Food/ packaging like fruit labels, bakery papers, wrappers for candy, chewing gum, meat and frozen fruits.
- Business machines like small computer key boards.
- Automotive applications like hard coat coatings for protecting of polycarbonate windows, mirrors and headlamps lenses, protecting of plastic trim, electronics, seat belt adhesive.
- Electrical fitting like cable accessories and insulators.

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