THE UNIQUE PHYSICO-CHEMICAL PROPERTIES OF SILOXANES

This factsheet explains what makes siloxanes unique, including how they are different from carbon-based materials, how they behave in the environment, and why the current PBT assessment criteria may not be suitable for them.

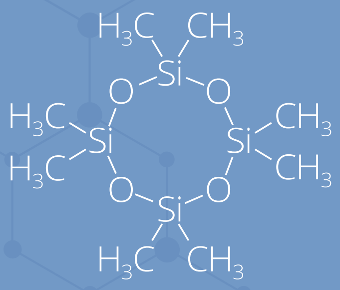
WHAT ARE SILOXANES AND SILICONES?

Siloxanes are characterised by a chain of alternating silicon and oxygen atoms. A long chain of siloxane groups is called a silicone or a silicone polymer. These are used in a variety of applications such as sealants, adhesives, coatings, plastics, cosmetics, medical devices, hygiene products, food contact materials, and many other industrial applications. Siloxanes differ in molecular weight, shape and functional chemical groups attached to the silicon-oxygen backbone.

Siloxanes are critical building blocks for all silicone products.

$[\mathrm{Si{-}O}]_n$

Siloxane
functional group



Octamethylcyclotetrasiloxane (D4)

Silicone polymers are specialty products that are used in small amounts in hundreds of applications where their special performance is needed. They are used as adhesives, they create flow, they insulate, and they have excellent mechanical/optical/thermal resistance among many other properties. Due to their molecular structure, silicones can be manufactured in many forms:

- solids
- liquids
- semi-viscous pastes
- greases
- oils
- rubber

Silicone polymers are typically liquids of varying viscosity. They may be linear or branched, but are individual polymer strands. Structuring of the polymer can occur by cross-linking the individual chains. Cross-linking is accomplished by synthesising polymers with functional groups on the chain that either react with each other or with moisture in the atmosphere. Cross-linked silicone polymers can have very different properties, depending on the degree of cross-linking:

WHAT ARE THE UNIQUE PHYSICO-CHEMICAL PROPERTIES OF SILICONES?

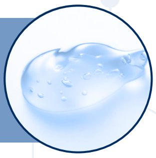
Silicone materials offer a host of useful characteristics (both physical and chemical) including:

- Wide range of thermal stability (high and low temperature)
- Resistance to oxidation, ozone, UV exposure
- Low surface tension (good wetting, spreading flow and antifoaming)
- Good dielectric properties
- Water repellency (hydrophobicity)
- Low flammability
- High gas permeability
- High compressibility and shear resistance
- Adhesive or dehesive properties
- Softness/flexibility

LIQUIDS

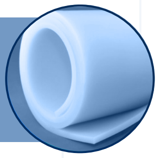
(SILICONE OILS, SILICONE-POLYETHERS)

GELS
lightly cross-linked – free flowing or pourable



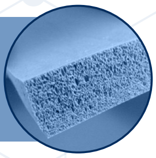
(SILICONE GEL)

RUBBER
higher degree of cross-linking – may be reinforced (i.e. silica)



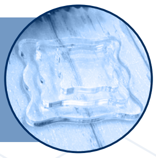
(SILICONE RUBBER)

FOAM
highly cross-linked and reinforced
(i.e. silica, acrylics)



(SILICONE FOAM)

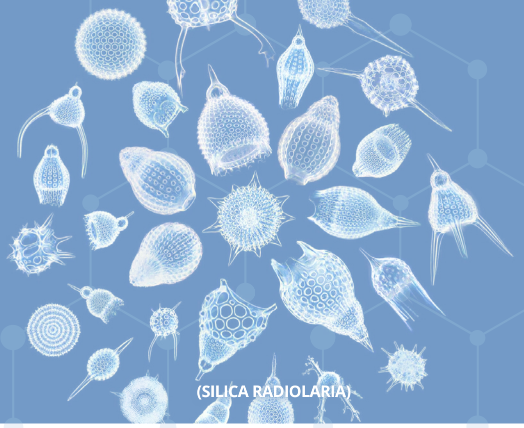
HARDCOATS



(SILICA ACRYLICS)

SILICON CHEMISTRY

Silicon is a chemical element (Si) widely distributed on earth in various combinations with oxygen only (silica) or oxygen and other elements (silicates). Silicon is the second most abundant element on the earth's crust after oxygen (approximately 28% by mass) and it naturally forms long-lived, stable compounds. In many biological systems (microorganisms, invertebrates and certain plant species) silica is an essential element of skeletal or mechanical structures.


(SILICA RADIOLARIA)

SILICON CHEMISTRY IS FUNDAMENTALLY DIFFERENT FROM CARBON CHEMISTRY

The backbone of inorganic silicon and oxygen atoms drives the unique properties of this chemistry set which makes them distinctly different from carbon chemistry.

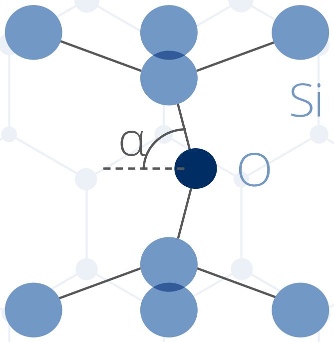
	Structural Backbone	Overall structure	Molecular Weight	Boiling Point (°C)	Vapor Pressure (mmHg)
D4	Si-O-Si	cyclic	296	176	1.6
Heneicosane	C-C-C	linear	297	360	8.7x10^{-5}
18-Crown-6	C-C-O-C	cyclic	264	350	6.7x10^{-5}

Although in the same group in the periodic table, silicon has a greater chemical affinity for oxygen compared to carbon. This difference is evidenced by the stronger bonds (higher bond energies, higher bond angles, and shorter than expected bond lengths) associated with the silicon-oxygen bond as compared to the carbon-oxygen bond. The silicon-oxygen bond angle confers a particular geometry, which allows rotation around the bond and leads to a more linear arrangement of the silicon-oxygen-silicon system.

The nature of the silicon-oxygen bond makes siloxane molecules like D4 flexible, which results in weak interactions between other siloxane molecules. This is illustrated by the lower surface tension, viscosity and higher vapor pressure of siloxanes compared to hydrocarbons of similar molecular weight.

Silicon has a moderate ability to form bonds with hydrogen. Carbon, on the other hand, has a very high affinity for hydrogen, with which it forms very strong, stable bonds.

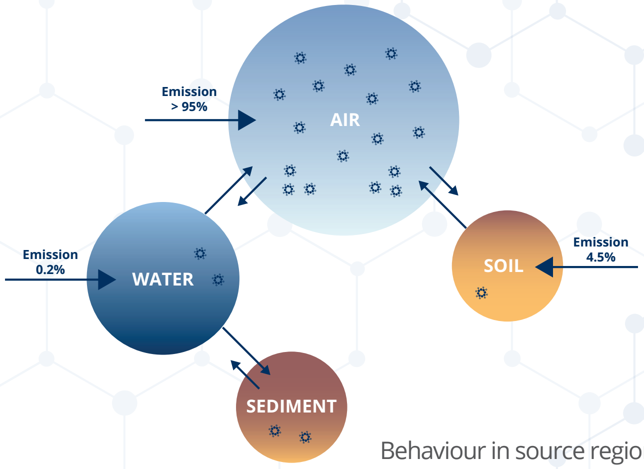
The large size of the silicon atoms makes the silicon-silicon bond poor, whereas the carbon-carbon bond is well known for its strength (graphite and diamond). Silicon does not form analogue structures to graphite or diamond.



CHEMICAL REACTIVITY OF SILOXANES AND THEIR ENVIRONMENTAL BEHAVIOUR

The most important siloxane building block is the dimethyl-siloxane group. This group comes along with unique physico-chemical properties, based on the large size (10 atoms per unit) and only a moderate ability to accept hydrogen bonds. These characteristics lead to differences in their capacity to interact with the environment such as water and organic carbon in soil/sediment and lipids in biota, compared to carbon-based hydrophobic organic compounds.

Consequently, siloxanes possess a combination of solubility and partitioning properties that influence their distribution in the environment, or effects on biota, which are significantly different from carbon-based materials.



Behaviour in source regions

Siloxanes do not back deposit in remote regions

THE CHALLENGE IN ASSESSING THE BEHAVIOUR OF SILOXANES IN THE ENVIRONMENT

Fundamental intrinsic properties of the siloxane molecules, such as vapour pressure and partition coefficient, need to be considered when assessing the environmental behaviour of siloxanes, as these are unique to siloxanes compared to other volatile hydrophobic chemicals such as organochlorine substances or polycyclic aromatic hydrocarbons.

For example, the assessment of octamethylcyclotetrasiloxane (D4), a low molecular weight cyclic siloxane, was done by using the guideline tests, criteria and mathematical models developed based on organochlorine chemicals. The guideline test systems cannot be used for non-water soluble and highly volatile substances and need to be adapted to non-standard tests that handle the substance in fully enclosed systems. These non-standard test systems form an artificial environment and may influence the test result just by the nature of the test system (i.e survival in Daphnia/Fish studies etc.).

The models do not take into consideration the vapour pressure together with other partition coefficients (e.g. Henry's Law Constant). Therefore, these criteria and models do not accurately characterise the environmental behaviour of siloxanes (Xu et al., 2016).

The criteria for identification and classification of Persistent, Bioaccumulative and Toxic (PBT) substances have been largely developed on the basis of organochlorine chemicals, and they do not reflect the combination of properties of siloxanes.

The Bioconcentration Factor (BCF) is a measure of the accumulation of a chemical in biota from the surrounding water environment and it is used to predict biomagnification in the field. The Biomagnification Factor (BMF), the ratio of a chemical concentration in one organism to that in its food or prey, is also used to provide an estimate of biomagnification in a food chain (increasing concentration of a chemical in a food chain). BMF may be measured in either laboratory tests or using field monitoring data. The BMF provides more information than BCF regarding accumulation of poorly soluble, lipophilic substances by aquatic organisms.

The BCF was developed based on the properties of hydrophobic and highly lipophilic substances like polychlorinated biphenyls (PCB) or polycyclic aromatic hydrocarbons (PAH) that do not undergo metabolism. Siloxanes do not behave in the same way. They are hydrophobic and lipophilic substances but they biodilute, therefore do not undergo biomagnification, largely due to the fact that they are metabolised.

Because of the differences between carbon and silicon-based substances highlighted above, the environmental effects of siloxanes cannot be predicted by traditional methods that were developed for carbon-based materials. The traditional PBT assessment criteria are, for that reason, not appropriate for assessing the risk of siloxanes on the environment.

Siloxanes are indispensable building blocks in the production of silicones. Silicones are enabling substances for many aspects of modern life: from life enhancing medical technologies, to renewable energy and energy saving solutions, to empowering the digital economy to construction and transportation.

To better understand the little-known and impressive benefits of silicones, and learn more about the value of silicones please visit globalsilicones.org.

GSC
GLOBAL SILICONES COUNCIL

References

Xu, S.; Warner, N.; Durham, J.; McNett, D. 2016. Critical review and interpretation of environmental monitoring data for cyclic methylsiloxanes: Predictions vs. empirical measurements in air and sediment. Posterbeitrag SETAC Europe 26th annual meeting 22-26 May in Nantes.