Silicone Science

www.PCC.asia

What is silicone?

Silicone has Si-O-Si bond in its molecule structure and Oxygen or Carbon is chemically linked on the side of Si molecule. etc.

“Silicone” is artificially synthesized compound making use of sand as a major raw material which can be found everywhere on earth crust and it is generally referred to as the whole family of organic Si compound containing Si combined with organic unit. By the way, “Silicon” means simply a Si atom looks like a dark-grey metal and we differentiate it with ‘silicone’ by deleting ‘e’ in the spelling. It is generally used for Silicone wafer in semi-conductor. The main ingredient of silicone is ‘Si’ and we often call silicone as a organic Si polymer. Si takes the second largest portion on earth after Oxygen and exists as a silica state, which is the major component of sand or glass. Although we can find Si, Chloride abundantly in the nature, silicone is synthesized with metal silicon that is made by silica by deoxidization at high temperature (about 3,000 degree C) in electric furnace. Therefore, silicone production requires a lot of electric energy; it can be produced in countries where the cost of electricity is very low. Conventionally, metal silicon was produced in U.S., Norway, France, Canada, but Norway, Brazil, China are increasing the quantity recently because of low cost electricity. As silicon atom lies in the same 4th family with carbon in the periodic table of elements, silicone compound can make similar chemical deployment as carbon-hydrogen organic compounds. But their features and functions are quite different due to the difference of basic chemical cohesion caused by the size of atom and electro negativity, etc. Silicon (Si) itself is an inorganic material but silicone compound has similar molecular characteristic as other organic compound. For example, low molecular weight silicone can be distilled and synthesized to higher molecular weight compound, which can be easily molded, adhered, coated. As the cohesion between silicon (Si) and oxygen is stable, silicone can be transformed to many highly polymerized compounds. Many thermoplastic, thermosetting polymers contains carbon(C) in its structure. But silicone is the unique material, which does not contain carbon in its main chain; therefore silicone has peculiar characteristics by the strong cohesion of inorganic chain and the flexibility of organic unit attached on the side chain of silicon (Si). Thus, silicone is widely applied to every industry with its unique characteristics with both organic features and inorganic features. Furthermore, silicone has superior heat resistance, weatherability, chemical stability, electric insulation than carbon-containing polymers; it has thousands of applications as a highly functional material. Silicone can be converted to Emulsion, Grease, Compound, etc from its basic form of silicone fluid, rubber, and resin. We can include the followings as a family of silicone: Silane Coupling agents, Polysilane, HMDS (Hexa Methyl Di-silazane), Polycarbosilane, Polysilazane, etc.

The main reason why silicone can be applied to a variety of industrial applications is because of the easy product designing. In other words, the diversity of molecular structure, variety of organic units attached to silicon (Si), lots of curing mechanism make it possible for the silicone to be used and applied widely in recent industrial needs.

a) Diversity of molecular structure, size, branch, density of crosslink, change of end-block unit, etc.
b) Variety of organic units, Methyl, Vinyl, Fluoro, Alkyl, Polyestere, Polyethere, Acryl, etc.
c) Lots of curing mechanism Peroxide, Addition, Ultra-violet, electron beam, etc.

www.PCC.asia www.SiSiB.com
Fax: +86-25-8468-0091
Tel: +86-25-8468-0092

The first step in the production of silicones involves the reduction of silica (SiO2) to silicon(Si) in an electric arc furnace. The silicone is then converted to methylchrolosilanes by a direct process reaction with methyl chloride in the presence of copper as a catalyst.

$(CH_3)_3SiCl$ - Trimethyl chlorosilane

CH_3Cl + Si ----> $(CH_3)_2SiCl_2$ - Dimethyl Dichlorosilane

CH_3SiCl_3 - Methyltrichlorosilane

The chlorosilanes react with water. Trimethyl chlorosilane is mono-functional, it reacts with water to form a dimmer.

It can also react with the surface of various materials such as fabrics, imparting water repellency and other properties. However, in the control of silicone polymer molecular weight, it is used as an end-blocking unit.

Dimethyl chlorosilane is difunctional and react with water to form siloxane polymers.

Polymerization continues until stopped by the addition of end blocking trimethyl units.

The lower molecular weight polymers are fluids.

The higher molecular weight polymers are gums, which the viscoelastic rubbers are made through cross-linking mechanisms.

Methyltrichlorosilane is trifunctional and react with water to form oxygen cross-linkeded polymers, which may be used as the basis for rigid resins.

The silicon-oxygen linkage in the silicone polymer chain is the same strong Si-O-Si bond occurring in quartz, sand, which contributes the outstanding high temperature properties of the silicones and their resistance to oxidation by ozone, corona, and weathering.

On the other hand, organic polymer chains such as occur in organic rubber, often have double carbon-carbon bonds, which are quickly cleaved by ozone, ultraviolet light, heat and other environmental conditions.

www.PCC.asia www.SiSiB.com
Fax: +86-25-8468-0091
Tel: +86-25-8468-0092
June 2009

Two-sided Characteristics

The outstanding physical properties and diverse application of silicone is resulted by the peculiar molecular structure.

As silicone is the combined polymer between inorganic silicon(Si) and organic carbon compound, it shows inorganic characteristics such as heat stability, anti-friction, gloss, etc. and organic characteristics such as reaction, solubility, elasticity, adhesion, etc.

Because silicone is the combination between Carbon and Silicon(Si), silicone has anti-volatility features and because silicone is the complex combination among Oxygen, Carbon, Silicon, and Organic units, it shows releasing property, defoaming property, lubricating property, and di-electric property.

The followings are the summary of silicone characteristics.

- Double faced characteristics

  Organic features

  -Heat stability, Chemical stability, anti-friction, glossy

  Inorganic features

  -Reaction, solubility, elasticity, adhesion

- Inherent characteristics as a compound

  Lubrication, releasing, defoaming, di-eletric,weatherability, anti-ozon, etc

www.PCC.asia www.SiSiB.com
Fax: +86-25-8468-0091
Tel: +86-25-8468-0092
June 2009

Recently, the silicone technology and new development trend is slowly changing.

Silicone was originally specialty products used for specific applications but dimethyl silicone oil, silicone rubber and sealant has become generalized used for every industrial application.

In the process of silicone demand increase, we have to notice that new application and new market had been continuously searched by actual users and customers.

For example, LSR (Liquid silicone Rubber) was very special products used for specific application only but now it is used for almost every application, which had become generalized product.

And, we can find other examples like RTV technology for the protection of delicate electronic parts, sealant for structural glazing which enabled advanced design of building and degenerated organic silicone oil for fabric and cosmetic market.

Currently, the silicone product line made out of monomer reaches around 3,000 lines which was the result of various needs of customers and markets.

Another important fact for the new product development is that almost every product was not the result of silicone makers but the result of cooperation between actual users and silicone makers.

As there are hundreds of markets and thousands of applications, the knowledge and technology of silicone makers cannot follow the market trend of each application.

Therefore, new technology and dew product development should be made by the exchange of market and technical information together.

Actually, when we see the case of Japan, silicone users teach silicone makers for the market status, trend, quality requirement, etc.

We can see the evidence if we think almost 90% of silicone related patents were provided by the users.

Therefore, it is not desirable to install or modify production facility to be adjusted for the existing silicone products.

It is not an easy process for the small countries to get the exact product for the production facility or customer's specific requirement as they depend on the imported products which is generalized for some market group.

Silicone makers are trying to reduce costs by the rationalization or reduction of production line which protect the development of new specialty product for special application.

www.PCC.asia www.SiSiB.com
Fax: +86-25-8468-0091
Tel: +86-25-8468-0092

Therefore, it is very urgent for the silicone users to enhance silicone application technology and basic silicone technology so that they can develop and modify their own product formulation which can give them superior competitiveness against other companies.

It is also important for the silicone suppliers to have more close relationship with silicone users for the exchange of silicone related technology and in some cases it is needed to have trial batch equipment.

Another important global technical trend is the harmonizing and blending silicone with other organic material.

In order to reduce the defects of silicone and introduce the merits of organic raw material, silicone can increase its market demand.

Modification of thermoplastic material or thermoset material with silicone can be one of the efforts for the new future market.

There are many development in Japanese companies for the research of raw material focused patents not application focused.

Acryl silicone sealant, acryl silicone paint can be one of the example.

In accordance of this trend, the demand for reactive silicone - organo silane, alkoxy silane, oligomer oil, resin, etc- is increasing.

Especially, silane is demanded for the polyolefin polymerization and for the process of anti-biotic intermediate.

There are many companies supplying functional products for the needs of specialized application

The trend for the new technology, new product, and new material will be continuing.

www.PCC.asia www.SiSiB.com
Fax: +86-25-8468-0091
Tel: +86-25-8468-0092

1. Silicone?

Silicon is the second most abundant element in the earth's crust, comprising around 28% of it. It is not found in its elemental form but occurs mainly as oxides and silicates. In contrast to carbon, silicon-silicon bonds are uncommon. Natural silicon-carbon bonds are extremely rare but they can be created synthetically.

Silica is a three dimensional network of silicon dioxide, most commonly encountered as sand. Silica exists in crystalline and amorphous forms. Silica is chemically resistant at ordinary temperatures but can undergo a variety of transformations at high temperatures (greater than 500 deg. C) and pressures. The industrial production of amorphous silica requires temperatures of 500 deg. C and much higher temperatures are required to produce crystalline silica.

The prolonged inhalation of crystalline silica dust is associated with silicosis. Amorphous silica is much less pathogenic than crystalline forms. Conversion of amorphous to crystalline silica cannot occur at body temperature. High purity amorphous silica is used as a reinforcing agent to increase the tear resistance of silicone rubbers used in medical devices and implants.

Silicones are synthetic polymers and are not therefore found naturally. They have a linear, repeating silicon-oxygen backbone akin to silica. However, organic groups attached directly to the silicon atoms by carbon-silicon bonds prevent formation of the three-dimensional network found in silica. These types of compound are also known as polyorganosiloxanes. Certain organic groups can be used to link two or more of these silicon-oxygen backbones and the nature and extent of this crosslinking enables a wide variety of products to be manufactured. The most important materials used in medical implants are fluids, gels and rubbers (elastomers) whose physical and chemical properties include, amongst others, a high degree of chemical inertness, thermal stability and resistance to oxidation.

Silicone fluids (oils) are usually linear chains of polydimethylsiloxane (PDMS) which have a wide range of chain lengths and molecular masses. Cyclic polydimethylsiloxanes also occur and are important intermediates in the manufacture of the linear chain fluids. They are virtually insoluble in water.

Silicone gels have lightly cross-linked polysiloxane networks, swollen with PDMS fluid to produce a cohesive mass. The PDMS fluid is not chemically bound to the crosslinked network but is retained only by physical means, as water is in a sponge, and there is a tendency for the fluid to "bleed". The degree of cross-linking and amount of fluid affects the physical properties of the gel and the rate at which fluid "bleeds" from it. Once suitably cross-linked, silicone gels retain their form without external containment.

Silicone elastomers are extensively cross-linked and contain little free PDMS fluid. The barrier coating of breast implant shells is a special silicone elastomer which is selected specifically to minimize migration of PDMS from the implants. The tensile strength and tear resistance of silicone elastomers may be increased

www.PCC.asia www.SiSiB.com
Fax: +86-25-8468-0091
Tel: +86-25-8468-0092
June 2009

by addition of amorphous silica which is usually pre-treated with organosilicon compounds to enable it to be tightly incorporated into the polymer network.

2. The measurement of silicone

Silicone materials contain a relatively high proportion of silicon (in general, about 20% by mass for PDMS). Quantitative measurement of silicon has therefore proved to be a convenient means of determining the silicone content of industrial materials. This method has the advantage of greater simplicity, in comparison with methods specific to silicone groups. The analyses must make allowance for the possibility of high levels of adventitious contamination of reagents and equipment arising from the wide natural distribution of silicon in the form of silica and silicates.

While in industrial applications it is convenient to measure silicon as a way to determine the silicone content of materials, it does not follow that the same proportions apply in the human body: in other words, you cannot assume that silicon is an indicator of silicone in the body. Silicon levels by themselves should not be interpreted as an accurate measure of silicone content in body fluids.

3. The use of silicone

There is widespread use of silicone materials and it is difficult to avoid exposure to them. Silicone is incorporated into medicines; used in food processing (for example, canning and ready meals); used in a wide range of medical devices; used as putty and sealants. The use of silicone oils in food processing and food contact can give rise to systemic exposure to small chain silicone components which are known to be absorbed through the gastrointestinal tract. Silicone is used in domestic and personal products such as cleaning solvents, hand cream, hair and skin products, and antiperspirants. It may be absorbed orally or through the skin and absorption can be measured on a scale from 'minimal' to 'well'.

Silicone is also incorporated in some medicines and medical devices. For example, silicone oil is commonly used as a lubricant in syringes and blood giving sets. People with insulin dependent diabetes are exposed to small but regular doses of silicone oil, resulting in a large, cumulative exposure to silicone over a period of time. Silicones are also used during surgery to repair retinal detachment.

www.PCC.asia www.SiSiB.com
Fax: +86-25-8468-0091
Tel: +86-25-8468-0092
June 2009

Periodic Table of the Elements

Silicon
Atomic Number: 14
Atomic Symbol: Si
Atomic Weight: 28.086
Electron Configuration: [Ne]3s23p2

Uses

Silicon is one of man's most useful elements. In the form of sand and clay it is used to make concrete and brick; it is a useful refractory material for high-temperature work, and in the form of silicates it is used in making enamels, pottery, etc. Silica, as sand, is a principal ingredient of glass, one of the most inexpensive of materials with excellent mechanical, optical, thermal, and electrical properties. Glass can be made in a very great variety of shapes, and is used as containers, window glass, insulators, and thousands of other uses. Silicon tetrachloride can be used as iridize glass.

Hyperpure silicon can be doped with boron, gallium, phosphorus, or arsenic to produce silicon for use in transistors, solar cells, rectifiers, and other solid-state devices which are used extensively in the electronics and space-age industries.

Hydrogenated amorphous silicon has shown promise in producing economical cells for converting solar energy into electricity.

Silicon is important to plant and animal life. Diatoms in both fresh and salt water extract Silica from the water to build their cell walls. Silica is present in the ashes of plants and in the human skeleton. Silicon is an important ingredient in steel; silicon carbide is one of the most important abrasives and has been used in lasers to produce coherent light of 4560 A.

Silicones are important products of silicon. They may be prepared by hydrolyzing a silicon organic chloride, such as dimethyl silicon chloride. Hydrolysis and condensation of various substituted chlorosilanes can be used to produce a very great number of polymeric products, or silicones, ranging from liquids to hard, glasslike solids with many useful properties.

www.PCC.asia www.SiSiB.com
Fax: +86-25-8468-0091
Tel: +86-25-8468-0092

Silicone sealant has superior properties than other organic sealant with durability, weatherability, heat resistance, low temperature stability, water repellency, etc.

These properties are caused by the basic molecular structure of organo-polysiloxane which is the major raw material of silicone sealant.

The first sealant was acetic acid type and then oxime type was developed later.

And 2-part type RTV sealant was also developed.

The major industry of sealant is construction with more than 80% portion.

Starting sealing two sides of structures, blocks, silicone sealant recently is used widely in automotive, aircraft, vessel, vehicles, general housing, etc.

Recently high functional sealant is developed as the development of new construction engineering method like curtain wall building.

Silicone sealant is cured by the moisture in the air and then become elastic rubber.
Silicone sealant is made of organo polysiloxane as the major ingredient mixed with inorganic fillers, cross-linkers, additives.

Silicone sealant is divided by the cross-linkers used.

1 part type

Acetic acid type	Good adhesion, clarity, Bad acetic smelling, corrode metal
Oxime type	No smelling Corrode similar type metal only
Alcohol type	No smelling, No corrosion, good adhesion with mortar, but late curing
Amid type	No corrosion, Smelling of amid
Amine type	No corrosion, Smelling of imid
Mastic type	No primer needed, good adhesion Less bulky with solvent

2 part type; less elasticity, high tensile, good adhesion late in curing in closed room, high temperature

SiSiB® SILANES
Power Chemical Corporation Limited

www.PCC.asia www.SiSiB.com
Fax: +86-25-8468-0091
Tel: +86-25-8468-0092
June 2009

◆ **1 part silicone sealant**

1 part silicone sealant is packaged in cartridge or tube and is used with compressing the packages.

When exposed to air, it cures by the reaction with moisture which cures from outside to inside by releasing special byproducts.

The curing time depend on the moisture and temperature.

The major applications are

Between glasses, glass suspension
Between glass and chassis
Sealing around stainless steel
Sealing marble
Sealing Bath tube

◆ **2 part silicone sealant**

2 part silicone sealant is consisted of main material, curing agent, pigment and used after mixing.

According to the mixing ration difference, the properties does not always same.

2 part silicone sealant has low modulas and high elongation properties.

The major applications are

Sealing metal curtain wall
Sealing concrete curtain wall
Sealing of woods
Sealing between glass and chassis

The consumption of 2 type silicone sealant is increasing especially in sealing curtain wall in high building.

www.PCC.asia www.SiSiB.com
Fax: +86-25-8468-0091
Tel: +86-25-8468-0092
June 2009

Silane is a very important material as a coupling agent.

It works as a mediate between mineral filler and rubber, plastic and keeps the reinforcing effect even exposed to water for a long time which is the main role of filler.

Silane has very unique material by having 2 functions as shown in its chemical structure.

R1-Si- (OR)3

R1 means organo-functional group which react with many polymers (amino,mercapto, methacryloxy, vinyl epoxy).

OR means hydrolysable alkoxy group which is located at the other end side.

Generally, the water on the surface of filler hydrolyzes ALCOXY GROUP and produces

SILANOL and the SILANOL reacts with water on the filler surface. Therefore the bond is made between filler and polymer.

It is said that 1% of Filler weight will be most effective.

It can be either input during or before the compounding process.

Silane is widely used in the process of making glass-reinforced plastic and mineral intermixed high quality rubber product.

www.PCC.asia www.SiSiB.com
Fax: +86-25-8468-0091
Tel: +86-25-8468-0092
June 2009

Silicone oil is used as a releasing agent because of its low surface tension and no adhesion property.

It is used to get easy demolding in plastic or organic rubber parts production.

In general, silicone oil is used as a mixture with water to make emulsion which is low cost and no smell and no danger of fire or flame.

Sometimes silicone oil is diluted by hydro-carbon solvent such as toluene, zylene, gasoline, kerozine, etc.

Or halogenated hydro carbon can be used such as chloroform, carbon tetrachloride, trichloro ethylene.

But you cannot use silicone oil as a releasing agent in case the demolded parts needs to be painted as a second process because the paint is not applied due to the repellant property it has.

The merits of silicone oil as a demolding agent are

* It penetrate into every delicate corner of the mold due to low surface tension property.

* It does not produce smell, smoke in the process of organic rubber at high temperature due to heat resistant property.

Please note that you should not use silicone oil as a releasing agent in the production of silicone parts because silicone has the tendency to adhere together with similar material.

www.PCC.asia www.SiSiB.com
Fax: +86-25-8468-0091
Tel: +86-25-8468-0092
June 2009

Silicone grease is a non-flowable libricant made by mixture between silicone oil and many additives such as metal soap, etc.

Silicone grease has many unique features like heat stability, anti-abrasion, solvent-resistance, water-stability but extreme high and low temperature performance is the major difference from other organic greases.

Therefore it is widely used as an essencial lubricant in small cars, conveyers in cold-storage building, or starter motor, wipe motor in electric applicances, refrigerater, fan, washing machine, or optical instruments, precise measuring equipment etc.

In fact, many automotive parts where high temperature stability is important will be the major application of silicone grease.

If we say silicone grease is used as a dynamic lubricant, silicone compound can be used as a static lubricant, sealing agent or protective coating agent.

Silicone compound means a mixture between silicone oil and SiO_2 powder and other ingredients.

It is widely used with its special characteristics, hydrophobicity, rust-proof, anti-corrosion, lubricity, tight sealing, electric insulation.

When we mix silicone oil with metal dioxide, we can get good heat conductive compound which can be applied to heat radiating plate in transister, diod as a filling material.

www.PCC.asia www.SiSiB.com
Fax: +86-25-8468-0091
Tel: +86-25-8468-0092
June 2009

About silicone resin

We can get silicone resin by cross linking METHYL TRICHROLOSILANE which is produced by the direct synthesis between CH_3Cl and metal silicon(Si).

It is a cured state and hard as a glass.

If you want some flexibility, you can add DIMETHYL DICHLOROSILANE.

Uncured and low molecular weight TRIMETHYL CHROLOSILANE is very hard in room temperature, but it turns fluid state at over 90 degree C which is an ideal molding compound that can be used at low pressure.

It can be used as a protecting material for very delicate parts such as semiconductive module.

It is also used in connecting area of highly delicate electric wires by transfer molding because it is supplied as granule type.

It increases the durability of many electronic products because of excellent qualities - electric insulation, heat resistance, flame retardency, moisture resistance, etc.

Silicone resin also acts as a binder in the production of delicate ceramic parts.

If we input silicone resin into many natural fillers (Glass fiber, Asbestos, Silica, Quarts, Metal Oxide, etc) by 5-20%, the flowability of the compound is increases which make Transfer molding, Compression molding possible.

About 5 minuits of molding process at 150 – 180 degree C, the molded parts is transferred to heat treating process.

At this heat treating process, silicone resin transforms into silica which is a part of ceramic.

Of course, there is no weight loss and the outer delicate line is perfect.

Another effective application of silicone resin will be painting and coating.

If we need to apply paint or varnishes to the parts facing extremely hard environmental conditions such as exhaust pipe in diesel engine, outer parts of vessel, we can get desirable performance when we apply ALKYD PAINT made out of silicone resin.

There is no yellowing even in extreme salty, ultra-violet, high temperature environment.

Application of silicone resin

www.PCC.asia www.SiSiB.com
Fax: +86-25-8468-0091
Tel: +86-25-8468-0092

Silicone resins are characterized by their three-dimensional structure based on silicone and oxygen linkages. The siloxane-linked backbone gives silicone resins their special properties, such as high temperature resistance and outstanding weatherability. In this respect silicone resins are quite different from organic resins. Historically, silicone resins have established a permanent place in the market, not only as "pure" resins for ultra-high temperature resistance, but also in the form of combination resins, such as silicone polyesters. Specially adapated binders are used for distinct areas of application:

Resins to make construction materials water-repellent
Low surface tension resins for release properties
Resins for high temperature and corrosion resistance
Resins for the decoration of high temperature household appliances
Weather-resistant resins applied by coil coating

www.PCC.asia www.SiSiB.com
Fax: +86-25-8468-0091
Tel: +86-25-8468-0092
June 2009

In general, Dimethyl silicone fluid is mainly used as a defoaming agent.

As the surface resistivity of dimethyl silicone fluid is too low (20 dynes/cm), only 10 gram of silicone oil is enough to defoam in thousands liters of liquid.

We may sometimes get low productivity, loss of times in the production of chemical products by the creation of much foams in the process.

As silicone is inherently inert and not harmful to human body and only minimum Q'ty is used, it doesn't make pollution or impact on the change of property for the final product.

Therefore, dimethyl silicone fluid is often used as a ingredient for anti-indigestion tablet and used in brewing, making detergents, etc.

Furthermore, with the function of foam control, it is often used in the process of plastic foam production.

Also it is used in polyurethane foam making mattress, automobile sheet, chair, packaging material, etc.

www.PCC.asia www.SiSiB.com
Fax: +86-25-8468-0091
Tel: +86-25-8468-0092