1

Materials

1.1 History

The history of silicone rubber, its development and technological progress has been described (1–3). Its first commercial development was in 1944. Pioneering research on silicon opened the door to the development of silicone polymers and silicone rubber. The substitution of two methyl groups on silicon was present in the first examples of silicone rubber and still is the predominant organic group in commercial silicone rubber today (1).

Silicone rubbers have filled a need in the marketplace because of their combination of unusual properties not found in other rubbers. The alternating inorganic main-chain atoms of silicon and oxygen, and the two pendant organic groups, primarily methyl, provide strong chain bonds, backbone flexibility, ease of side-group rotation, and low inter- and intramolecular forces (1).

Also, industrial organosilicone materials, their environmental entry and their predicted fate have been described in a monograph (4). Furthermore, a comprehensive overview of the issues of organosilicon compounds has been presented. Commercial products, such as sealants, adhesives, and coatings are reported (5, 6).

1.2 Properties

1.2.1 *Tracking and Erosion Resistance*

Silicon rubber (SR) also offers excellent electrical performance under contaminated environments. However, a pristine silicone rubber has low thermal properties and this may cause tracking and erosion failure due to severe dry band arcing and ohmic heating on the insulating surface (7).

The effect of material thermal characteristics on the tracking and erosion resistance of silicone rubber filled with micron-sized alumina trihydrate, aluminum nitride and boron nitride particles was investigated (7). Composites with different loading were synthesized by dispersing the particles in pristine room temperature vulcanized (RTV) silicone rubber and an IEC 60587 inclined plane test (8) was conducted to evaluate tracking and erosion resistance. Apart from physical parameters and leakage current, an infrared thermal imager was used to measure the surface temperature distribution during the course of the inclined plane test. Experimental results showed tracking and erosion resistance is significantly enhanced with addition of boron nitride particles followed by alumina trihydrate.

Aluminum nitride composites exhibit a poor tracking and erosion resistance, similar to pristine silicone rubber. It has been concluded that the addition of boron nitride composites improves the ability to impede the tracking and erosion process, the reasons being better thermal stability and enhanced thermal conduction in the discharge region. On the other hand, infrared analysis revealed that thermal accumulation is remarkably higher in aluminum nitride composites, which promotes dry band arcing and results in tracking and erosion failure (7).

To improve the tracking and erosion resistance performance of addition-cure liquid silicone rubber (LSR) without alumina trihydrate, addition-cure LSR samples with different fumed silica mass fraction and platinum catalyst concentration were prepared (9).

The tracking and erosion resistance performance of the samples were evaluated. Also, the thermal decomposition products were detected. Based on the comparative analysis of thermal decomposition characteristics, the morphology, crystal structure, and improvement mechanism were assessed.

The results of this study showed that both increasing the concentration of the platinum catalyst and the mass fraction of fumed silica can improve the tracking and erosion resistance performance, whereas the former was more effective. Further analysis indicated that the platinum catalyst played a very important role in the thermal decomposition process of addition-cure LSR. Increasing the platinum catalyst content can not only promote the crosslinking reaction between the methyl groups, but also can suppress backbone decomposition (9).

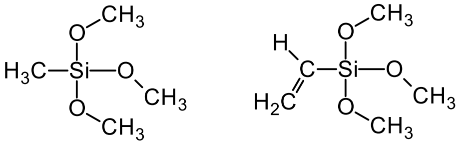
1.2.1.1 Impact of Various Fillers

The influence that various fillers having different sizes, from 0.3 μm to 18 μm, and surface modifications (unmodified, modified by the material supplier and *in-situ* modified during compounding) have on the erosion resistance of high temperature crosslinked silicone rubber composites was analyzed. The particles used were aluminium trihydrate, alumina (Al_2O_3) and silica (SiO_2). The main focus was on aluminium trihydrate fillers since they have the ability to release water at elevated temperature.

By a simple water storage test under defined conditions the water uptake for different composites was analyzed to assess the effectiveness of an *in-situ* modification. The inclined plane test according to IEC 60587 (8), and the high voltage, low current dry arc test according to IEC 61621 (10), were used to determine the erosion resistance of the different samples.

For the inclined plane test, an adapted evaluation model was applied. This test is known to have a wide scatter in the case of material formulations, which are on the borderline of passing or failing the test and therefore show substantial erosions on certain samples. The scatter could be reduced by evaluating the eroded volume by using samples only, which showed a limited erosion length. It was found for aluminium trihydrate, that larger particles show slightly better results than smaller particles. This can be explained by the formation of boehmite AlO(OH) for the larger particles, which causes a release of the bound water over a wider temperature range.

This effect could be confirmed by thermogravimetric analysis (TGA). The surface modification of the particles with vinyltrimethoxysilane and methyltrimethoxysilane, c.f. Figure 1.1, did not improve the erosion resistance significantly, but reduces the water uptake to a large extent, which is advantageous for the retention of the hydrophobicity. In order to achieve a low erosion rate, high filler loadings are essential (11).



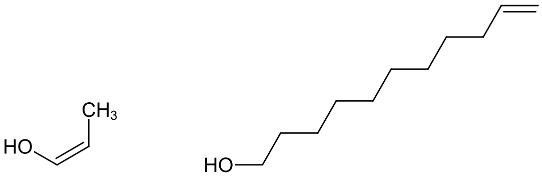
Methyltrimethoxysilane Vinyltrimethoxysilane

Figure 1.1 Methyltrimethoxysilane and Vinyltrimethoxysilane.

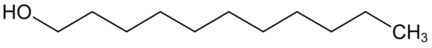
1.2.2 *Enhancing Strength*

Silica is the most widely used filler to reinforce LSR, but the high viscosity of a LSR/silica suspension significantly limits its processing flexibility (12).

To balance the processability and the reinforcing efficiency of LSR/silica systems, two kinds of enols, i.e., propenol and 1-undecylenyl alcohol, and a saturated alcohol, 1-undecylic alcohol, were employed to modify the silica surface. The compounds used here are shown in Figure 1.2.



Propenol 1-Undecylenyl alcohol



1-Undecyl alcohol

Figure 1.2 Alcohols.

Modified silica samples were prepared via surface esterification of silica with alcohols by the reflux method. The calculated amount of precipitated silica (Rhodia Z-142), xylene, and alcohol were added into a reaction flask. Then a solid-liquid extractor containing sufficient CaH_2 and a condenser with a $CaCl_2$ drying tube were mounted on the reaction flask. The mixture was heated to 160°C and refluxed for 24 *h*. Finally, the samples were filtered and washed with ethyl acetate at least five times and dried in a vacuum oven at 120°C for 8 *h*.

The carbon contents, alkoxyl surface densities, and bound rubber contents of various silica samples are shown in Table 1.1.

Table 1.1 Properties of various silica samples (12).

Modifier	Carbon content /[%]	Alkoxyl surface density /[$\times 10^6 mol\, m^{-2}$]	Bound rubber content /[%]
None	0.08	—	0.81
1-Undecylic alcohol	4.12	1.73	0.52
1-Undecylenyl alcohol	4.80	2.02	0.54
Propenol	1.40	2.16	0.59

Obviously, the bound rubber content is largely reduced after silica surface modifications, suggesting that silica poly(dimethyl siloxane) (PDMS) interaction is effectively lowered by silica surface modification. Comparing different modifiers, there is not much difference between 1-undecylic alcohol modified silica and 1-undecylenyl alcohol modified silica, while bound rubber content for propenol modified silica is a little higher. It seems that modifiers with higher carbon chain lengths are more effective in lowering the PDMS silica interactions. Though propenol has a little higher density on the silica surface, it is the combined effect of grafting density and modifier chain length that determines the effect of silica surface modifications.

Various rheological tests were carried out to investigate the processability as well as filler networking and the crosslinking processes of the modified systems.

Polymer/filler composites are known to exhibit a complex rheological behavior that reflects interactions among components in the system. In PDMS/hydrophilic silica suspensions, there are strong interactions between PDMS and silica and among silica, mainly via hydrogen bonding, which would cause a drastic increase in viscosity or reduction in the mobility of PDMS, consequently deteriorating the processing properties of LSR.

The effect of silica surface modification on viscosity of the suspension is believed to be determined by the combined effects of the type of grafting enol (saturated or unsaturated), grafting carbon content (or carbon chain length), and grafting density

Tensile tests were also adopted to verify the reinforcing effect. Tensile strength of various crosslinked LSR systems as a function of silica content are shown in Figure 1.3. Also, the tensile elongation break of various crosslinked LSR systems as a function of silica content are shown in Figure 1.4.

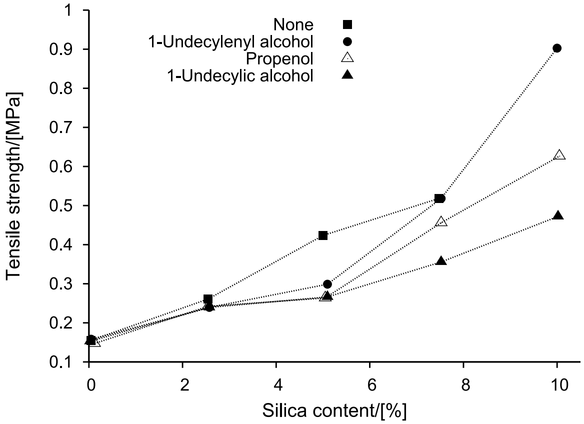


Figure 1.3 Tensile strength of various crosslinked LSR systems as a function of silica content (12).

The investigated systems follow a similar trend: First, the elongation increases gradually with the content of silica, and then decreases because the rigidity of the filler begins to dominate the property. Comparing the systems reinforced with different kinds of silica at the same silica content, their orders of elongation at break (from high to low) are listed as follows: 1-Undecylenyl alcohol modified system, untreated silica reinforced system, propenol-modified system, and 1-undecylic alcohol modified system (elongations of the last two systems are very close). For instance, at the silica content of 2.5%, where tensile strengths of various systems are similar, the average elongations of the reinforced rubbers at the above sequence are 268%, 249%, 231%, and 225%, respectively.

In summary, it was found that surface modification of silica by 1-undecylenyl alcohol could significantly reduce the viscosity of its

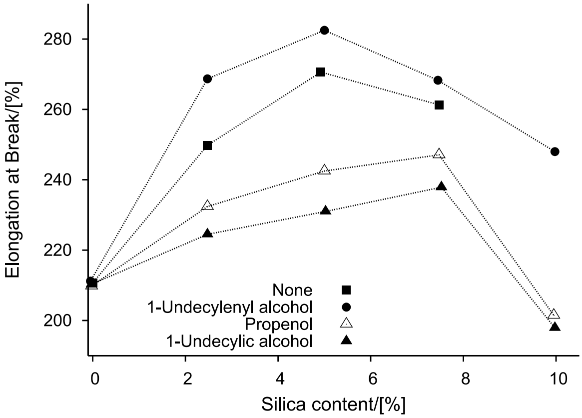


Figure 1.4 Tensile elongation break of various crosslinked LSR systems as a function of silica content (12).

suspension with LSR. Also, the mechanical strength of LSR could be largely enhanced by six times with 10% modified silica (12).

1.2.3 Surface Treatment

1.2.3.1 Prevention of Microwrinkles

Attempts have been made to prepare a homogeneous film on a PDMS surface and to eliminate microwrinkles from the surface (13). Hydroxy groups were generated on a PDMS surface using different methods.

Because the hydroxylation process changes the chemical composition of the PDMS surface, resulting in a cracked surface, the selection of the best method for surface treatment with minimized surface microwrinkles and cracks was tried.

The results obtained from scanning electron microscopy showed that using the pulsed ultraviolet-ozone radiation method with a controlled duration time, ozone treatment, continuous ultraviolet-ozone treatment using a glass filter, and water media in ultraviolet-ozone treatment was more effective than other methods evaluated in the study to prevent microwrinkles.

Also, the results obtained from contact angle measurements and attenuated total reflectance Fourier transform infrared (FTIR) spectroscopy revealed that the ultraviolet-ozone treatment in the presence of a water medium created more hydroxy groups in comparison to other methods (13).

1.2.3.2 *Antifouling Surfaces*

Biomimetic Antifouling Surface. Despite the distinct advantages of PDMS for biomedical applications, because of its hydrophobic nature, this material suffers from non-specific protein adsorption and platelet adhesion and activation when used as a blood-contacting material (14).

To confer hydrophilicity and biomolecules repelling characteristics, well-defined and high-density poly(2-hydroxyethyl methacrylate) brushes were synthesized via surface-initiated atom transfer radical polymerization (SI-ATRP) on the PDMS substrate (14).

First, the PDMS surface was activated using an ultraviolet/ozone wet treatment in water media to introduce hydroxy moieties without scarifying the surface property, resulting in a crack-free SiO_2 surface. Then, 3-(2-bromoisobutyramido)propyl(trimethoxy)silane, c.f. Figure 1.5, the active atom transfer radical polymerization initiator, was immobilized on the ultraviolet/ozone-treated PDMS surface to prepare a thin layer of hydrophilic poly(2-hydroxyethyl methacrylate) brush on PDMS substrate, exhibiting excellent protein and platelet resistance. Poly(2-hydroxyethyl methacrylate) brushes supply a biomimetic feature by combining antifouling properties due to hydrophilic characteristic with bioactive properties resulting from the presence of high density hydroxy groups, which can be subsequently used for the conjugation of biomolecules.

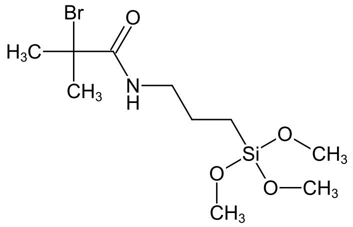


Figure 1.5 3-(2-Bromoisobutyramido)propyl(trimethoxy)silane.

The results of the study indicated that grafting of poly(2-hydroxyethyl methacrylate) chains on the PDMS surface enhances the surface wettability, which leads to a decrease in non-specific protein adsorption and platelet adhesion compared to the bare PDMS substrate. The adhered platelets on the poly(2-hydroxyethyl methacrylate)-tethered PDMS substrate maintain their normal round morphology. In addition, the conjugated gelatin macromolecules on the tethered poly(2-hydroxyethyl methacrylate) chains promote the adherence and growth of human umbilical vein endothelial cells via ligand-receptor interactions (14).

Antifouling Marine Paints. Antifouling marine paints are topcoats intended to prevent the attachment of animals or plants to the lower parts of the hulls of ships (15). They are used for reasons of safety, maintaining the maneuverability of ships, reducing fuel consumption, combating corrosion and weighing-down of structures.

Biofouling is a major problem resulting from the immersion of materials in marine environments. The prevention of this phenomenon represents a considerable maintenance cost. Specifically, the formation of biofouling occurs during immersion in seawater, where a layer of organic and inorganic molecules is adsorbed to the surface of the material extremely rapidly. This layer of adsorbed material, or biofilm, serves as a mediator for the adhesion of the bacteria present in suspension in the marine environment.

This colonization of the surface by marine bacteria is rapid and a stationary state is reached after a period of a few hours to a few days. Finally, other marine organisms colonize the surface, the adherent bacteria recruiting these other organisms. All these live organisms attached to the surface constitute the biofouling or fouling. The adhesion of marine fouling concerns any structure immersed in the sea: ships, pipelines, cooling towers and circuits, harbor structures, marine sensors, aquaculture systems, etc. The damage caused is considerable and diverse. Specifically, the structures become coated, for example, with organisms which have a negative effect on the performance levels of the structures. In particular, for the hulls of ships, the incrustation of various marine organisms increases the friction between the hulls of the ships and the seawater, which reduces the speed and can lead to greater fuel consumption (15).

Thus, the bottom of a ship which is not protected by an antifouling system can, after less than six months spent at sea, be covered with

150 *kg* of fouling per square meter. In order to avoid economic loss, and also in order to more successfully inhibit corrosion phenomena, antifouling paints, the objective of which is to prevent or notably reduce the soiling due to the incrustations of marine organisms, are applied to the immersed parts of the structures exposed to water.

The principle of antifouling paints is based on the controlled release of the active substance at the interface between the surface and the seawater. The effectiveness of the paint is maintained as long as the concentration of active substance released at the surface is effective and regular. Most antifouling paints therefore contain a biocidal product which is most commonly an organometallic compound (based on tin, copper or zinc) or an organic compound (fungicide, algicide, bactericide) which prevents adhesion of the marine soiling owing to the toxic activity thereof (15).

Tributyltin, which is very effective, was therefore the biocide most commonly used in antifouling paints, but this product, its degradation molecules and its metabolites proved to be seriously and sustainably polluting. For these reasons, the International Maritime Organization prohibited the use of tin-based antifouling paints. The antifouling paints used today are mainly based on copper-containing compounds and/or on synthetic chemical compounds, but also are based on silicone polymers. With regard to the copper-based paints, although they are less toxic than tin salts, they are virtually always formulated with a massive proportion of cuprous oxide. However, they are effective only against the marine fauna, and, in order to combat the growth of algae, it is essential to add herbicides, which can pose new threats to the environment.

These silicone-based paints forming an antifouling coating are very innovative:

1. They are completely friendly to the marine environment: no metal waste, and
2. They improve the glide of ships, thus reducing by 1 to 5% their fuel consumption and therefore their greenhouse gas emissions.

An antifouling topcoat based on a silicone elastomer can contain fluids which improve the antifouling effect, in particular (15):

1. Methylphenylpolysiloxane oils (16),

2. A hydrocarbon-based liquid compound, for example a polyolefin,
3. A plasticizer,
4. A lubricating oil,
5. Liquid paraffins and waxy masses of the petrolatum type,
6. A thermoplastic polymer such as poly(vinyl chloride),
7. A vinyl chloride/vinyl acetate copolymer, or
8. Cationic, anionic, nonionic or amphoteric surfactants.

In order to form the silicone elastomer coating, the silicone formulations generally used involve a silicone oil, generally a reactive poly(dimethyl siloxane) with hydroxylated endings, which optionally prefunctionalize with a silane so as to have alkoxy ends, a crosslinking agent and a polycondensation catalyst, conventionally a tin salt or an alkyl titanate, a reinforcing filler and other optional additives such as bulking fillers, adhesion promoters, and dyes (15).

The catalysts which are used are based on tin, titanium, or amine or compositions. Catalysts based on tin and on titanium are very effective (17).

1.2.3.3 Bilayers for Gas Separation

Thin film composites of poly(2-hydroxyethyl methacrylate) and poly(methyl methacrylate) (PMMA) chain-tethered poly(vinylidene fluoride) (PVDF)-PDMS were prepared as a gas separation membrane (18). PDMS was coated on the PVDF support using a dip coating method. Poly(2-hydroxyethyl methacrylate) and PMMA were then grafted on PVDF-PDMS substrate by atom transfer radical polymerization.

The PVDF-PDMS-poly(2-hydroxyethyl methacrylate) and PVDF-PDMS-PMMA trilayer membranes were studied by attenuated total reflection FTIR spectroscopy, scanning electron microscopy (SEM), atomic force microscopy (AFM), water contact angle measurement, and X-ray photoelectron spectroscopy (XPS). The results of separation tests indicated that the CO_2/N_2 selectivity of PVDF-PDMS-poly(2-hydroxyethyl methacrylate) and PVDF-PDMS-PMMA thin film composites increased by ~2 and ~3 times, respectively, compared to the solvent-extracted PVDF-PDMS support (18).

1.2.4 Adhesion Properties

1.2.4.1 Combinations with Thermoplastic Polymers

The application field of combinations of thermoplastic polymers and LSR is remarkably wide, ranging from household consumers to the automotive sector (19). For the application of such combinations, the adhesion is a deciding factor.

In the case of LSR, tempering for improving its mechanical properties is used. However, there is no profound knowledge on annealing the combinations, thus making the influence on adhesion unclear.

The influence of different tempering temperatures (80°C, 100°C, and 120°C) and times (1, 3, 6, and 9 *h*) on the adhesion between the thermoplastic poly(butylene terephthalate) (PBT) and poly(amide) 12) and LSR was studied. The results showed that post-tempering influences the single components.

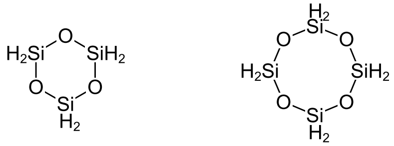
In the case of PBT, post-crystallization already occurs at 80°C, which is reflected, for instance, by increasing the degree of crystallinity by about 22%. LSR showed a post-crosslinking and the release of volatile components. Analyzing the tempering impact on adhesion, the peel resistance of LSR and PBT decreased around 23% at 80°C. The covalent bonds at the boundary layer were weakened due to the post-crystallization and the release of volatile components.

To identify the volatile components of the LSR, a gas chromatography coupled with mass spectrometry measurement was done. The test specimens were tempered in hermetic bags to catch the volatile components.

The volatile components mainly consisted of silicon-oxygen connections, such as siloxanes, silanes, and silanols, such as trimethylsilanol, disiloxane, cyclotritrisiloxane, and cyclotetrasiloxane, c.f. Figure 1.6.

During tempering, the volatile components are released. The amount of volatile components increased during varying tempering times, but their chemical composition remained the same while altering the temperature (19).

Trimethylsilanol Disiloxane



Cyclotritrisiloxane Cyclotetrasiloxane

Figure 1.6 Volatile silicon-oxygen components (19).

1.2.4.2 Octamaleamic Acid-POSS

The addition of octamaleamic acid-polyhedral oligomeric silsesquioxane (POSS), c.f. Figure 1.7, nanoparticles to SR composites was investigated for enhancing the adhesion properties of reinforcing fibers (20). The content of octamaleamic acid-POSS was examined as the experimental parameter.

As reference a 5 *phr* silica-filled SR compound was used. The peroxide curing characteristics of composites was determined using differential scanning calorimetry (DSC) and a moving die rheometer.

It was found that octamaleamic acid-POSS retarded the curing time and decreased the crosslinking density. DSC analysis indicated that the crosslinking reaction started at a lower temperature as the octamaleamic acid-POSS concentration increased. The thermal mechanical analysis results showed that the melting point decreased with the addition of octamaleamic acid-POSS.

The crosslinking enthalpy and the curing onset temperature of SR composites are shown in Table 1.2.

The crystallinity of SR decreased with increasing octamaleamic acid-POSS content. The thermal stability of SR composites obtained from TGA apparently improved with the addition of octamaleamic acid-POSS. Scanning and transmission electron microscopy showed that the octamaleamic acid-POSS distribution was homogeneous at

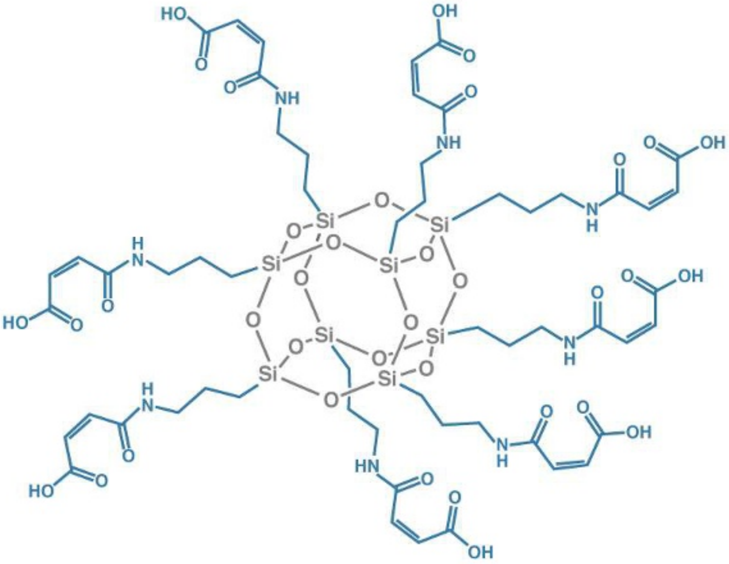


Figure 1.7 Octamaleamic acid-POSS.

Table 1.2 Crosslinking enthalpy and curing onset temperature of silicon rubber composites (20).

POSS added /[*phr*]	Curing enthalpy/[*J g*$^{-1}$]	Curing onset temperature/[°C]	Curing peak temperature/[°C]
0	13.0	150.7	189.3
1	7.4	151.4	181.2
3	8.5	151.8	183.4
7	7.6	145.3	187.8
10	8.2	145.5	188.2

lower contents, but some agglomerates were seen when the content of octamaleamic acid-POSS increased.

Tensile tests showed that comparable mechanical properties were achieved for SR/octamaleamic acid-POSS composites with respect to reference composite.

It could be demonstrated by H-adhesion tests that the utilization of octamaleamic acid-POSS in the SR composites improved the adhesion of the matrix to a Rayon fiber (20).

1.2.4.3 Improvement of Adhesion Strength

Polymeric hard/soft combinations consisting of a rigid, thermoplastic substrate and an elastomeric component offer many advantages for plastic parts in industry (21). Manufactured in one step by multi-component injection molding, the strength of the thermoplastics can be combined with sealing, damping or haptic properties of an elastomer. Bonds of self-adhesive LSR on high performance thermoplastics, such as poly(ether ether ketone) or poly(phenylene sulfide), are especially interesting for medical applications due to their outstanding resistance properties.

To ensure good adhesion between the two components, surface treatments from an atmospheric pressure plasma jet and a Pyrosil® flame were applied. The chemical changes on the thermoplastic surfaces were verified by water contact angle measurement and XPS.

A plasma treatment causes a decline in water contact angle, indicating the formation of functional groups, especially −OH, on the surface. XPS measurements confirm the increase of oxygen on the surface. Thus, the number of functional groups on the thermoplastic surface is enlarged by plasma treatment, leading to stronger bonding to the organofunctional silanes of the self-adhesive silicone rubber.

A thin layer of silanol groups is created by the Pyrosil flame on the thermoplastic substrates, which could be verified by XPS. A hydrophilic behavior of the coated surface is noticed. Both surface modification methods lead to enhanced adhesion properties of self-adhesive LSR on thermoplastic surfaces. This could be confirmed by 90° peel tests of the injection-molded composites, which led to an increase in the peel force by the surface modification techniques used (21).

1.2.4.4 Tackiness Reduction

A millable silicone rubber is widely used for producing rubber components because it can be mixed with a coloring agent with a simple device such as a twin-roll mixer and can be molded by simple equipment such as a press, and especially because its shape can be retained even in an uncured state. It is widely used in extrusion molding of tubes, gaskets, etc. (22).

However, the unique tackiness that the surface of a cured silicone rubber has is likely to cause the problem of blocking of surfaces of its molded products (22). Forming minute irregularities on the surfaces can prevent the blocking, and in molded products formed using a mold, the blocking can be easily prevented by roughening the surface of the mold. However, in extrusion molding and coating which do not use a mold, it is difficult to control the surface state.

A silicone rubber composition has been described that has improved moldability, in particular, extrusion moldability, while ensuring that a cured product obtained therefrom has sufficient strength. The silicone rubber composition contains (22):

A 100 part by mass base polymer consisting of a poly(organo siloxane diol) whose viscosity at 25°C is 1 to 100 $Pa\,s$ and a poly(organo siloxane) whose viscosity at 25°C is 0.2 to 40000 $Pa\,s$, with a ratio of the last compound of 20 to 100% by mass to the whole composition, the base polymer having a viscosity of 5 to 20000 $Pa\,s$ at 25°C and having an alkenyl group content of 0.001 to 0.3 $mmol\,g^{-1}$. Furthermore, a 10 to 50 part by mass silica powder whose specific surface area is 50 to 400 m^2g^{-1}, a 1 to 10 part by mass organosilazane, and a catalytic amount of a curing agent.

Several special examples for such compositions have been detailed (22). When such a composition is extruded at a rate of 2 $m\,min^{-1}$ by a screw extruder and thereafter cured into a tubular cured product, the tubular cured product preferably has, on a surface, 1 to 300 pieces/0.01 mm^2 granular protrusions whose maximum diameter measured in a scanning electron microscopic image is 0.1 μm to 30 μm. A SEM photograph (5000X) of the surface of the silicone rubber extrudate is shown in Figure 1.8.

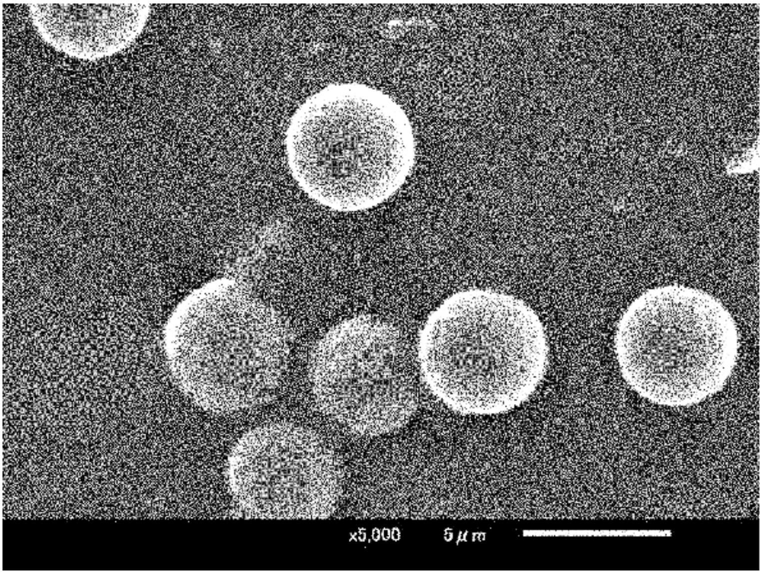


Figure 1.8 SEM photograph of a tubular cured product (22).

1.2.5 Pressure-Sensitive Adhesive Film

Silicone pressure-sensitive adhesives have the excellent heat resistance, freeze resistance and electrical properties inherent in silicone and maintain adhesion without impairing these properties (23). Thus, they can be widely used as pressure-sensitive adhesives where a high level of reliability is required.

Typical silicone pressure-sensitive adhesive compositions contain (23,24):

1. A diorganopolysiloxane having at least two alkenyl groups in a molecule,
2. An organopolysiloxane containing $R_3SiO_{1/2}$ units and $SiO_{4/2}$ units in a molar ratio of the $R_3SiO_{1/2}$ unit to the $SiO_{4/2}$ unit of from 0.6 to 1.7, wherein R is a monovalent hydrocarbon group having 1 to 10 carbon atoms,
3. An organopolysiloxane having at least two silicon-bonded hydrogen atoms in a molecule,
4. An inhibitor,
5. A hydrosilylation catalyst, and
6. A solvent.

The silicone pressure-sensitive adhesive compositions may be applied to micro gravure coatings in order to obtain a thin pressure-sensitive adhesive layer on a substrate film. However, the aforementioned silicone pressure-sensitive adhesive compositions cannot form the pressure-sensitive adhesive layer exhibiting proper adhesion and good anti-scratch properties on the substrate film (23).

A silicone composition has been developed that exhibits proper viscosity and can form a pressure-sensitive adhesive layer that exhibits proper adhesion and good anti-scratch property on a substrate film (23). Another objective was to provide a pressure-sensitive adhesive film whose pressure-sensitive adhesive layer exhibits proper adhesion and a good anti-scratch property.

The compositions contain the ingredients shown in Table 1.3. These components will be explained in detail later on.

The alkenyl groups in component (A) can be exemplified by vinyl, allyl, butenyl, pentenyl, hexenyl, and heptenyl groups and are preferably vinyl groups. Component (A) can be exemplified by dimethylvinylsiloxy-endblocked dimethylpolysiloxanes, dimethylvinylsiloxy-endblocked dimethyl siloxane-methylvinyl siloxane copolymers, trimethylsiloxy-endblocked dimethyl siloxane-methylvinyl siloxane copolymers, partially branched chain dimethylpolysiloxane with molecular chain ends terminated by dimethylvinylsiloxy and trimethylsiloxy, trimethylsiloxy-endblocked partially branched chain dimethyl siloxane-methylvinyl siloxane copolymers.

Component (B) is another diorganopolysiloxane having at least one alkenyl group in a molecule. The alkenyl groups in component (B) can be exemplified by vinyl, allyl, butenyl, pentenyl, hexenyl, and heptenyl groups and are preferably vinyl groups. The non-alkenyl Si-bonded organic groups in component (B) can be exemplified by alkyl groups and aryl groups and are preferably methyl and phenyl groups.

The pressure-sensitive adhesive film is similar to that shown in Table 1.3.

The silicone composition exhibits a proper viscosity and can form a pressure-sensitive adhesive layer that exhibits proper adhesion and good anti-scratch property on a substrate film. Furthermore, the pressure-sensitive adhesive film has a pressure-sensitive adhesive

Table 1.3 Ingredients for pressure-sensitive adhesive compositions (23).

No.	Description
A	Diorganopolysiloxane having at least two alkenyl groups in a molecule, and having a viscosity at 25°C of from 10,000 to 1,000,000 *mPa s*, in an amount of from 60 to 80 mass based on a mass of the composition
B	A diorganopolysiloxane having at least one alkenyl group in a molecule, and being raw rubber-like at 25°C or having a viscosity at 25°C of more than 1,000,000 *mPa s*, in an amount of more than 0%, but not more than 10% based on a mass of the composition
C	An organopolysiloxane resin containing $(R^1_3SiO_{1/2})_x(SiO_{1/2})$, where R^1 is halogen-substituted or unsubstituted monovalent hydrocarbon group free from an alkenyl group and x is a number from 0.5 to 1.0, in an amount of from 0.5% to 20%
D	An organohydrogenpolysiloxane having at least two silicon-bonded hydrogen atoms in a molecule, in a quantity that provides from 0.1 to 10 moles of the silicon-bonded hydrogen atoms in this component per 1 mole of the total alkenyl groups in the composition
E	Silica fine powder in an amount of from 0.5 to 5% based on a mass of the composition
F	A hydrosilylation catalyst in a quantity that accelerates hydrosilylation of the composition

layer exhibiting proper adhesion and good anti-scratch property (23).

The pressure-sensitive adhesive film is produced by applying the silicone composition onto the surface of the substrate film, and then forming a pressure-sensitive adhesive layer on the surface of the substrate film by curing the composition at room temperature or with heating. Curing with heat is preferable. Heating should be carried out at a temperature above 50°C, preferably within the range of 80 to 200°C (23).

1.2.6 Storage Stability

A composition prepared by blending a resin microparticulate catalyst with a mixture of an organopolysiloxane and a crosslinking agent cannot secure long-term storage stability in a mixed state at around room temperature depending on the type of the resin making up the resin microparticulate catalyst, so that problems of a significant increase in viscosity of the mixture and progress of curing of the mixture are caused (25).

In addition, it takes time to crosslink the mixture when curing the mixture by heating, so that the composition could show a low crosslinking reactivity. Until now, there has not been a technique for obtaining a silicone rubber composition that has both excellent storage stability in a mixed state and excellent crosslinking reactivity during heating.

A silicone rubber composition has been developed that contains an organopolysiloxane, a crosslinking agent, and a microcapsule type of catalyst that is made of microparticles of a resin and a crosslinking catalyst encapsulated in the microparticles.

Examples of the organopolysiloxane include an alkenyl group-containing organopolysiloxane, a hydroxyl group-containing organopolysiloxane, a (meth)acryl group-containing organopolysiloxane, an isocyanate-containing organopolysiloxane, an amino group-containing organopolysiloxane, and an epoxy group-containing organopolysiloxane.

The alkenyl group-containing organopolysiloxane is used as a main material for an addition curing type silicone rubber composition. The alkenyl group-containing organopolysiloxane is crosslinked by a hydrosilyl crosslinking agent in addition reaction with the hydrosilyl crosslinking agent. While proceeding even at room temperature, this addition reaction is promoted under heating. Thermal curing by this addition reaction is preferably performed at at 100–170°C.

The preparation of microcapsule type catalysts can be done as follows (25):

Preparation 1–1: A toluene solution of a platinum catalyst, containing 3% by mass of platinum metallic atoms, a coating resin for microparticulation, and toluene were mixed at a mass ratio of 0.6:5:95, and the thus-prepared solution was dropped into a water solution of a surface acting agent to prepare an emulsion. Then, the toluene was distilled and removed under reduced pressure and the emulsion was filtered to obtain microparticles for each catalyst that contain the coating resin and the platinum catalyst. As platinum catalyst, platinum chloride (IV) manufactured by Furuya Metal Co., Ltd. was used.

1.2.7 Thermal Stability

A platinum catalyst and a nitrogen-containing silane were introduced into a silicone rubber to improve the thermal stability (26). The effects of Pt and nitrogen-containing silane on the thermal stability and degradation mechanism of silicone rubber were investigated by thermogravimetry (TG), TG-FTIR spectrometry, SEM and other methods.

A significant synergism was found between Pt and nitrogen-containing silane for improving the thermal stability of the silicone rubber. When 6.67 *ppm* of Pt and 1.4 *phr* of nitrogen-containing silane were introduced, the temperature of 10% and 20% weight loss under nitrogen atmosphere were respectively increased by 36°C and 119°C. The residue weight at 900°C was doubled to 68% in the presence of the Pt/nitrogen-containing silane.

The synergistic mechanism might be that the nitrogen atom coordinated with Pt and improved the catalytic efficiency of Pt. Additionally, nitrogen-containing silane preserved the catalytic activity of Pt under air atmosphere. Thus, the Pt/nitrogen-containing silane efficiently catalyzed the thermal crosslinking and suppressed the degradation of silicone chains. Moreover, it revealed that the presence of Pt/nitrogen-containing silane protected silicone chains from oxidation. Thus, the unzipping depolymerization by silanol groups was reduced significantly (26).

1.2.8 Hydrophobed Pyrogenic Silica Filler

In order to prevent the undesirable influence of the silanol groups on the mechanical properties of a silicone rubber, it is necessary to render the surface of the pyrogenic silica hydrophobic (27).

A silicone rubber composition has been described, which is characterized by its containing a structurally modified hydrophobic pyrogenic silica as filler (28).

The silanized, structurally modified silica has vinyl groups fixed to the surface, hydrophobic groups such as trimethyl silyl or dimethyl silyl and/or monomethyl silyl groups additionally being fixed to the surface. The preferred properties are shown in Table 1.4.

Table 1.4 Preferred properties of the composition (28).

Property	Amount	
BET surface area	25 – 400	m^2g^{-1}
Average primary particle size	5 – 50	nm
pH	3 – 10	
Carbon content	0.1 – 10	%
DBP value	<200	%

The dibutyl phtalate (DBP) value in Table 1.4 is defined as the volume of dibutyl phtalate absorbed by 100 g of black pigment (29,30).

1.2.9 Superhydrophobic Materials

1.2.9.1 Superhydrophobic Surfaces

The fabrication of large-scale superhydrophobic surfaces for commercial applications is challenging due to certain limitations. A simple and inexpensive method has been developed to fabricate superhydrophobic surfaces on silicone rubbers (31).

Templates with different rough structures were prepared first. Silicon carbide particles of (63, 21, 15, and 10.5) μm in diameter were obtained by using test sieves of 80, 240, 600, 800, and 1200 *mesh*, respectively. A uniform layer of resin binder-epoxy resin was sprayed on the inner surface of a cubic mold with dimensions of $3cm\times3cm\times3cm$ after treating with a silane coupling agent

N-β-aminoethyl-γ-aminopropyl trimethoxysilane. The prepared silicon carbide particles were evenly sprayed on the inner surface of the mold and dried at room temperature. Then rough silicon rubber samples were prepared through a conventional molding process.Liquid silicone rubber was poured into the mold, the mold was taken off after consolidation, and thus silicone-rubber surfaces with different surface morphologies were obtained (31).

Rough microstructures were prepared on the inner surfaces of the molds and then sample superhydrophobic surfaces on silicone rubbers with different surface roughness were achieved using the standard molding process.

Furthermore, the effects of roughness on the wettability were investigated. The results showed that by controlling the roughness, the fabricated surfaces exhibited a static contact angle of 150.9° and a sliding angle of 8°. Finally, the property of hydrophobicity recovery for the silicone-rubber samples was studied. The surfaces of the samples could recover well after a sandblasting experiment. The proposed method is low cost, environmentally friendly and suggests promising industrial applications (31).

1.2.9.2 Flashover Characteristics

The influence of the low adhesion of superhydrophobic surface on flashover characteristics under wet conditions has been studied (32).

The samples are prepared as follows (32, 33):

Preparation 1–2: A sheet of glass with dimensions of 25 *mm* ± 75 *mm* ± 1 *mm* was put into a mold. The mold was 25 *mm* ± 75 *mm* ± 2 *mm*. Then, a liquid one-component room temperature vulcanized silicone rubber was poured into the mold. After the liquid silicone rubber cured, the common silicone rubber sample was acquired. The thickness of room temperature vulcanized coating was about 1 *mm*.

The common silicone rubber sample was similar to glass insulators coated by room temperature vulcanized coating. Then a mixture of ethyl acetate, liquid silicone rubber and SiO_2 nanoparticles was sprayed on the common silicone rubber sample. After the silicone rubber cured, a superhydrophobic surface was formed on the silicone rubber sample. Here, a superhydrophobic silicone rubber sample was acquired. The contact angle of superhydrophobic surface was larger than 150° and the sliding angle was less than 2°.

The flashover experiments were done with copper foils with 0.05 *mm* thickness that were used as electrodes. The copper foils were glued onto the samples. The distance between the electrodes was 2.5 *cm*. Then the electrodes were connected to an AC high voltage source. The mode of increase of voltage was a step-by-step test. If the samples withstood a voltage for 2 *s* without failure, the voltage would increase in steps of 0.2 *kV*. The voltage would be increased until flashover occurred. The whole process was recorded by a digital camera.

The flashover experiments were conducted under two different wet conditions. One was placing a constant volume droplet on the silicone rubber. The other one was that silicone rubber was wetted by salt fog.

It was found that the adhesion between water droplets and a superhydrophobic surface was very low, because of the presence of air cushion. Accordingly, water droplets were easy to slide on a superhydrophobic surface under the effect of electric filed. The sliding of droplets could provide a longer insulation path before the flashover occurred. The results of the study showed that the flashover voltage could be improved greatly on a superhydrophobic silicone rubber surface (32).

1.2.10 Thermally Conductive Materials

1.2.10.1 Layer-by-Layer Assembly

Thermally conductive silicone rubber composites used for heat removal from electronic devices have attracted great attention (34). A facile spin-assisted layer-by-layer assembly approach was used to fabricate highly thermally conductive multilayered silicone rubber/graphene films.

The films exhibit a highly ordered lamellar structure with the high orientation of graphene. This provides continuous thermally conductive pathways in the horizontal direction (34).

A multilayered film with 40 assembly cycles has the thermal conductivity of 2.03 $W(mK)^{-1}$ in in-plane direction. Moreover, the film can be highly twisted to any angle and has an elongation at break of 325%, which is rarely achieved in previously reported graphene-based multilayered films.

Even up to 500 stretch-recovery cycles at 50% strain, the change of the thermal conductivity was negligible, indicating the high durability, excellent flexibility and stretchability of the film. The films with high thermal conductivity and stretchability have potential applications in flexible electronics, wearable devices and electronic skin (34).

1.2.10.2 Boron Nitride

Boron Nitride Nanosheets. An efficient method was reported to fabricate boron nitride nanosheets using a sonication technique in mixed solvents (35). The functionalization of boron nitride nanosheets is performed by poly(dopamine). The boron nitride nanosheets showed good dispersibility in mixture solvent. And the functionalization of boron nitride nanosheets by poly(dopamine) can further improve their stability in water.

The morphologies of the boron nitride nanosheets and the poly(dopamine) modified compositions were characterized by AFM, SEM, and transmission electron microscopy, which confirmed the successful exfoliation and functionalization of boron nitride nanosheets. Furthermore, silicone composites were fabricated by adding boron nitride nanosheets and boron nitride nanosheets/poly(dopamine), respectively.

Compared with neat silicone (0.20 $W m^{-1} K^{-1}$), the thermal conductivity of silicone composite with 12% BNNSs poly(dopamine) increases highly by 90% to 0.38 $W m^{-1} K^{-1}$. The thermal stability of silicone/boron nitride nanosheets/poly(dopamine) composite is also improved.

The significantly improved thermal conductivity and thermal stability can be attributed to the good dispersion of boron nitride nanosheets/poly(dopamine) and a stronger interaction between the boron nitride nanosheets/poly(dopamine) surface and the silicone matrix (35).

Vertically Aligned Boron Nitride. Silicone rubber/vertically aligned boron nitride composites were prepared and the thermal conductivity of the composites was systematically investigated (36). The vertically aligned boron nitride molecules constructed effective vertical thermal conductive pathways in the SR matrix, and so the composites exhibited much higher through-plane thermal conductivity compared to the non-oriented composite.

The through-plane thermal conductivity of the composites reached 5.4 $kW\,m^{-1}K^{-1}$, which was 33 times higher than those of pure SR. In addition, the surface thermal infrared analysis also indicates that the vertically aligned SR/boron nitride composites possess an excellent heat transfer capacity during the heating and cooling processes (36).

1.2.11 Shape-Memory Materials

Shape-memory polymers are a kind of stimuli-responsive materials that can have physical transformation between their initial shape and temporary shape under certain external stimulus, such as heat, electricity, light chemical induction, and others. Shape-memory polymers have several advantages (37–39).

Many kinds of stimulation can induce the shape-memory effect. Furthermore, they can be designed in a broad range of ways, and have a flexible application (40).

A shape-memory polymer (SMP) contains two structure elements (41): A permanent network and reversible network. The permanent network is an elastic network, which is the part that keeps the permanent shape and drives recovery upon the application of a stimulus. The reversible network is able to counterbalance the load stored in the permanent network to fix a temporary shape and is sensitive to the stimulus-allowing recovery when the network is reversed.

The thermally induced SMP is mainly derived from the reversible network that undergoes a thermal transition such as a melting or glass transition (42, 43).

An electro-active SMP is a composite of thermally induced SMP materials and a conductive material, such as graphitized carbon black, or a metallic powder. The mechanism is similar to that of the thermally induced SMP. The conductive material increases the temperature of the system through the heat generated by the current, resulting in the shape recovery, so it has both conductive and shape-memory effects.

Four fillers were investigated in a study (40): Cornstarch, 1,10-decanediol, 12-hydroxystearic acid, and stearic acid. These compounds are shown in Figure 1.9.

By adding cornstarch, the sticky silicone is somewhat stiffened and starts to quickly set up from the inside out because of its moisture content. The other three fillers all can produce a shape-memory effect when they are blended with silicone rubber (40).

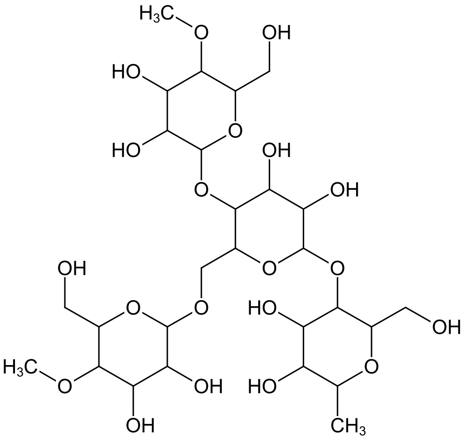
However, the performance is different. Compared with other samples, the 12-hydroxystearic acid blend sample does not perform well, its recovery is only around 80%. The decanediol silicon rubber blend showed the best performance; the next composition was stearic acid, with 12-hydroxystearic acid showing the poorest performance.

By mixing silicone rubber with 1,10-decanediol the shape-memory effect can be realized. The crystalline small 1,10-decanediol molecule could provide the reversible network. The silicone rubber part results in an elasticity. Samples can be stretched to 200% elongation and display good shape-memory properties. According to the shape-memory cycle test, a 50% 1,10-decanediol silicone rubber composition shows the best performance in terms of high fixity and recovery, and it displays good repeatability after several shape-memory cycles. By comparing 1,10-decanediol with other crystalline small molecules, 1,10-decanediol silicone rubber composition displayed the best performance (40).

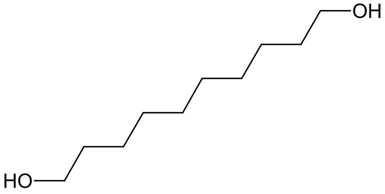
1.2.12 Thermally Conductive Grease

Electronic parts generate heat in use and, thus, the performance thereof lowers owing to the heat generation. In order to solve this problem, a variety of heat dissipation techniques have been employed. One of the ordinary methods includes placing a cooling member in the vicinity of a heat generation unit and bringing them in intimate contact with each other, thereby dissipating heat by efficient removal of heat through the cooling member.

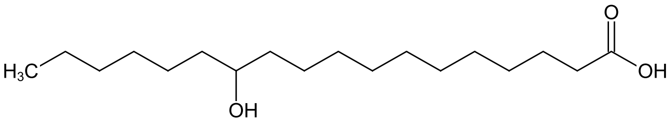
In this connection, however, if there is a space between the heat generation member and the cooling member, thermal conduction does not proceed smoothly because of the presence of air, which has poor thermal conductivity, so that the temperature of the heat generation member does not decrease satisfactorily. To prevent this, for the purpose of preventing the presence of air, heat dissipating



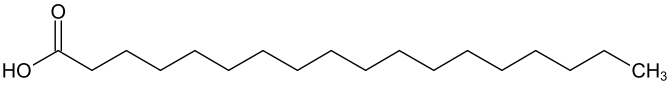
Cornstarch



1,10-Decanediol



12-Hydroxystearic acid



Stearic acid

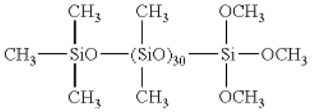
Figure 1.9 Fillers.

materials, heat-dissipating sheets or heat dissipating greases have been conventionally used, which are good at thermal conductivity and are able to follow the surface profile of the member.

A thermally conductive grease composition has been developed, which scarcely increases in hardness during high-temperature heating and has a minimized reduction in growth (44). The components of the composition are:

1. An alkenyl group-containing organopolysiloxane, examples are dimethylpolysiloxanes blocked with a dimethylvinylsilyl group at both ends.
2. A hydrolyzable methylpolysiloxane, trifunctionally terminated at one end,
3. A thermally conductive filler,
4. An organohydrogenpolysiloxane,
5. A triazine ring and alkenyl group-containing bonding aid, and
6. A platinum catalyst, and, if required,
7. An addition reaction inhibiting agent.

An example of a hydrolyzable methylpolysiloxane compound is shown in Figure 1.10. Examples of the organohydrogenpolysiloxane compounds are shown in Figure 1.11. A triazine compound is shown in Figure 1.12



$$CH_3{-}\overset{CH_3}{\underset{CH_3}{SiO}}{-}(\overset{CH_3}{\underset{CH_3}{SiO}})_{30}{-}\overset{OCH_3}{\underset{OCH_3}{Si}}{-}OCH_3$$

Figure 1.10 Hydrolyzable methylpolysiloxane (44).

1.2.13 Self-Healing Materials

Graphite nanoplatelets recently attracted attention as a viable and inexpensive material that can be used in many engineering applications, given the excellent in-plane mechanical, structural, thermal, and electrical properties of graphite (45–47).

Composites with carbon-based fillers show thermal stability, light weight, and a high thermal conductivity (48,49).

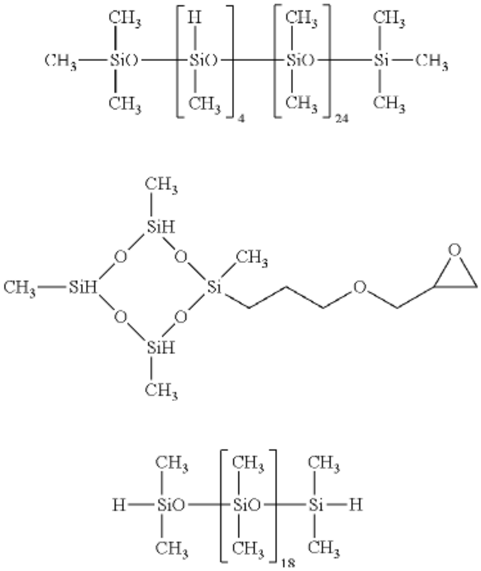


Figure 1.11 Organohydrogenpolysiloxanes (44).

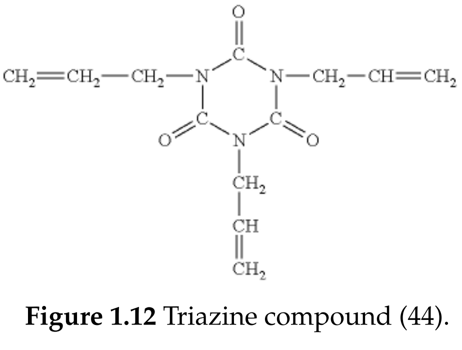


Figure 1.12 Triazine compound (44).

These properties suggested that integrating graphite nanoplatelets into SR might generate novel self-healing materials, which have multifunctional properties such as self-healing by thermal annealing and temperature activation of the electrical conductivity (50).

1.2.14 Flame Retardancy

To effectively enhance the flame retardancy of silicone rubber is a challenging task. Functionalized zirconium phosphate was prepared by the intercalation of 1,2,2,6,6-pentamethyl-4-(vinyldiethoxysiloxy) piperidine into a zirconium phosphate, c.f. Figure 1.13, and was employed to enhance the flame retardancy of addition-cured LSR (51).

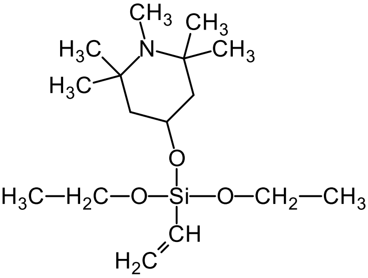


Figure 1.13 1,2,2,6,6-Pentamethyl-4-(vinyldiethoxysiloxy) piperidine.

The results of the study showed that addition-cured LSR had no rating in the UL-94 test (52,52) with the limiting oxygen index (LOI) value of 28.0%.

Functionalized zirconium phosphate could significantly improve the flame retardancy of addition-cured LSR. When only 4.0 *phr* functionalized zirconium phosphate was added, the LOI value reached 31.0% and the vertical burning test (UL-94) passed the V-0 rating. Moreover, compared to addition-cured LSR, the peak heat release rate and the total heat release of addition-cured LSR/functionalized zirconium phosphate decreased by 54.2% and 47.5%, respectively. The probable flame retardant mechanism of functionalized zirconium phosphate was mainly attributed to the synergism of the catalyzing carbonization and free-radical quenching effects. On the one hand, 1,2,2,6,6-pentamethyl-4-(vinyldiethoxysiloxy) piperidine suppressed the thermal degradation of silicone chains in the condensed phase and quenched the active free radicals in the gas phase by generating nitroxyl radicals.

On the other hand, ZrP promoted silicone chain self-crosslinking and the formation of the graphitized carbons, resulting in the formation of the compact and thermostable ceramic layer, which was a good barrier to protect the underlying matrix and inhibit the exchange of degradation products and oxygen (51).

In another study, the effect of POSS particles and the synergism of POSS and poly(melamine phosphate) on the thermal properties and flame retardancy of silicone rubber composites was investigated (53).

Flame retardant compounds for SR in the form of polyhedral POSS, containing both isobutyl groups and amino-propyl groups, or chloro-propyl groups or vinyl groups were tested. The structures are shown in Figure 1.14.

The silsequioxanes were incorporated into the silicone rubber matrix in a quantity of 3 and 6 parts by weight by the method of reactive stirring with the use of a laboratory mixing mill.

Based on TGA, FTIR and various SEM methods, the thermal degradation mechanism of non-crosslinked and crosslinked silicone rubber was elucidated. The effects of POSS, and POSS in a synergic system with melamine poly(phosphate), c.f. Figure 1.15, on the thermal properties and flammability of silicone rubber composites were reported.

Also, a mechanism of the flame retardant action has been proposed. The thermal degradation of silicone rubbers can proceed according to three reaction mechanisms: Unzipping, random scission of the Si−O bond in the main chain of polymer, and an external catalysis. PDMS containing silanol (Si−OH) or hydroxyl-alkyl-silanol (Si−R−OH) terminal groups, undergo thermal degradation by an unzipping mechanism. In the first stage of heating, the molecular weight of the polymer increases as a result of an intermolecular condensation process between the terminal and the silanol groups and interchain Si−O groups. A further increase in temperature causes a linear decrease in the polymer molecular weight as a result of the formation of cyclic siloxanes followed by their tearing off and passing to the gas phase of cyclic siloxanes, mainly trimers and tetramers.

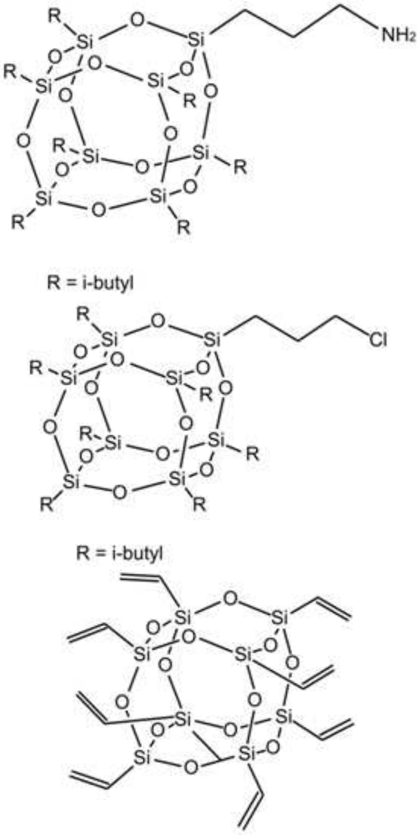


Figure 1.14 Polyhedral POSS compounds (53).

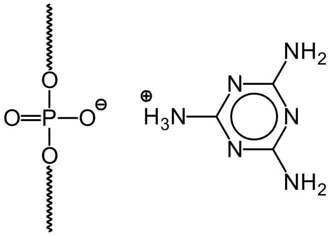


Figure 1.15 Melamine poly(phosphate).

It has been shown that POSS, especially with melamine poly(phosphate), considerably increases the thermal stability and decreases the flammability of the SR rubber composites (53).

1.3 Special Materials

1.3.1 Borosilicones and Viscoelastic Silicone Rubbers

Borosilicones, e.g., Silly Putty, have been known for 70 years, but their peculiar behaviors have remain unexplained. Experiments and theory were used to show that they are network liquids—dynamic macromolecules that appear elastic on short timescales but exhibit flow on longer timescales (54).

There are a number of techniques for incorporating boron in poly(organo siloxane)s (55) and consequently for producing silicone bouncing putties (56,57).

The reaction between a silanol group and a methoxy group on boron is a condensation reaction (54):

$$\begin{gathered} \mathrm{B(O{-}CH_3)_3 + HO{-}PMDS{-}OH} \rightarrow \\ \mathrm{B(O{-}CH_3)_2{-}O{-}PMDS{-}OH + CH_3OH} \end{gathered} \tag{1.1}$$

This reaction is reversible, so that alcoholysis accompanies condensation, and it normally reaches an equilibrium in which both reactants and products are present.

To drive the reaction toward condensation and borosilicone formation, the methanol must be removed. Simply allowing the methanol to evaporate is sufficient, but vacuum drying propels the reaction to completion far more efficiently. The condensation reaction is so rapid, even at room temperature, that vacuum removal of the methanol can cause the borosilicone to form within seconds (54).

Boron-containing crosslinking agents may be boric acid or a boric acid ester such as trimethyl borate, triethyl borate, triisopropyl borate, and tributyl borate (57). Due to their chemical structure, boron-containing crosslinking agents have three functional groups which can react with the silanol groups in the poly(organo siloxane). The use of a boron compound as the temporary crosslinking agent has an additional consequence: This material typically exhibits a remarkably high stiffness and resiliency in response to sudden impacts.

Chemicals bearing hydroxyl and carboxyl groups are particularly effective boron bridge-opening chemicals. Water, alcohols, polyols, silanols, and carboxylic acids are examples of chemicals bearing hydroxyl and carboxyl groups. Some chemicals are collected in Table 1.5 and some chemicals are shown in Figure 1.16.

Table 1.5 Boron bridge-opening chemicals (57).

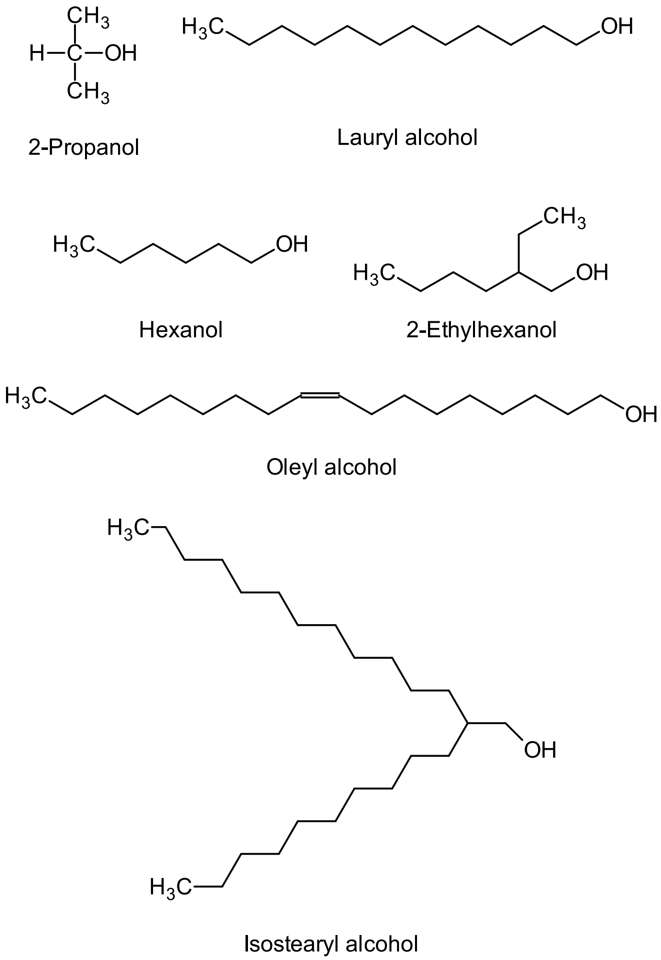
Primary alcohols	Carboxylic acids
2-Propanol	Acetic acid
Hexanol	2-Ethylhexanoic acid
Decanol	Lauric acid
2-Ethylhexanol	Stearic acid
Lauryl alcohol	Oleic acid
Stearyl alcohol	Isostearic acid
Oleyl alcohol	
Isostearyl alcohol	

Here, simple borosilicones were prepared by reacting a silanol-terminated poly(dimethyl siloxane) fluid HO-PDMS-OH and related compounds with the liquid boron compound trimethyl borate $B(OCH_3)_3$ (54). Examples of such poly(siloxane)s are shown in Figure 1.17.

Each borosilicone is a vast covalent network of silicone polymer chains joined by trifunctional boron crosslinks. At any instant, the borosilicone is a highly crosslinked elastic material. Because the boron crosslinks are temporary, however, the network evolves with time and the borosilicone exhibits a liquid behavior.

A simple borosilicone exemplifies a classic transient network model and behaves as a simple (Lodge) elastic fluid. Its measured moduli and viscosities fit those predicted by the transient network model and the Maxwell viscoelastic model: A spring in series with a dashpot, including the observed exponential relaxation processes.

When a borosilicone includes permanent crosslinks, however, it no longer behaves as a simple elastic fluid. Its measured moduli and viscosities fit those predicted by the fractional Maxwell viscoelastic model: A spring in series with a spring-pot, including the observed slower-than-exponential relaxation processes.



2-Propanol

Lauryl alcohol

Hexanol

2-Ethylhexanol

Oleyl alcohol

Isostearyl alcohol

Figure 1.16 Boron bridge-opening chemicals.

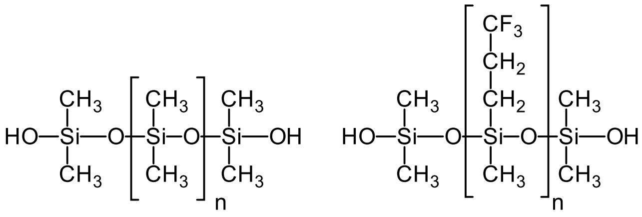


Figure 1.17 Silanol-terminated poly(siloxane)s.

Beyond the gelation threshold, a borosilicone becomes a viscoelastic silicone rubber (VSR). With a permanent network that spans the material coupled to a temporary network that also spans the material, the VSR is a network liquid piggybacking on a network solid. The fractional Zener viscoelastic model: An elastic spring in parallel with the fractional Maxwell model accurately predicts the measured moduli of VSRs. The temporary nature of boron crosslinks is due to exchange reactions. Because the mean lifetime of temporary crosslinks is a borosilicone's only significant timescale, it exhibits thermorheological simplicity (54).

1.3.1.1 One-Pot Synthesis

A one-pot synthesis procedure of polyborosiloxane resins by dehydrocarbon condensation of trimethyl borate with diphenylsilane in the presence of tris(pentafluorophenyl)borane as catalyst has been reported (58). The condensation process, which leads to the formation of Si−O−B linkages with a release of methane, was performed in a hydrocarbon solvent under mild conditions. The proposed reaction scheme is shown in Figure 1.18.

The so fabricated polyborosiloxane glassy product is halogen-free and has a low content of hydroxyl groups. High temperature decomposition of the polyborosiloxane resin yields a silicon-boron-oxycarbide ceramic with a high yield above 54%, when the process is carried out in a nitrogen atmosphere. The char yield is about 10% lower for thermal decomposition in the presence of air rather than in nitrogen.

The polyborosiloxane resins obtained by this process could find applications as high temperature adhesives, precursors to ceramic materials and halogen-free flame retardants (58).

1.3.1.2 Interfacial Adhesion

An attempt was made to improve the interfacial adhesion property between epoxy resin (EP) and addition-curable liquid silicone rubber (59).

As a surface treatment agent, borosiloxane oligomers were synthesized, and the major chemical structure was evaluated by gel per-

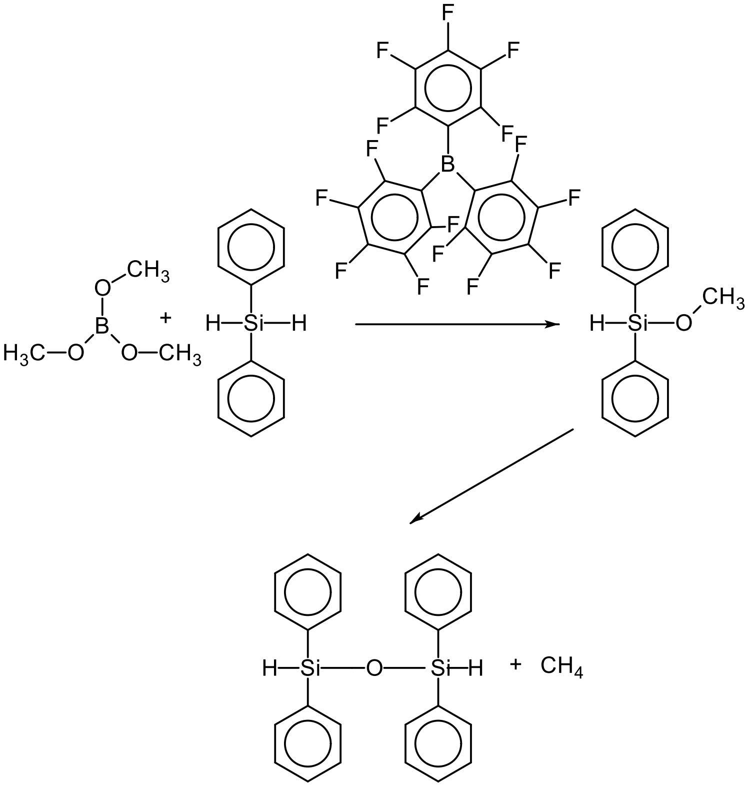


Figure 1.18 Formation of Si-O-Si bridges via exchange of functional groups and subsequent dehydrocarbon condensation (58).

meation chromatography, FTIR, nuclear magnetic resonance spectroscopy (NMR), and TGA.

Borosiloxane oligomers served as surface treatment agent for an epoxy resin to improve the interfacial adhesion characteristics of the epoxy resin and addition-curable liquid silicone rubber (59). The adhesion strength between epoxy resin and addition-curable liquid silicone rubber was measured by a pull-out test. The results indicated that the adhesion strength increased from 0.02 *MPa* for an epoxy resin/addition-curable liquid silicone rubber to 0.18 *MPa* for a borosiloxane oligomer-epoxy resin/addition-curable liquid silicone rubber, with the failure mode from epoxy resin posts dislodgement for epoxy resin/addition-curable liquid silicone rubber to rubber breakage for borosiloxane oligomers-epoxy resin/addition-curable liquid silicone rubber.

Furthermore, the adhesive mechanism was analyzed and it was concluded that the improvement of adhesion characteristics of the epoxy resin/addition-curable liquid silicone rubber through the oligomer surface treatment was a result of chemical and physical bonding. The borosiloxane oligomers acted as binder by reacting with amino groups on the surface of the epoxy resin through the active epoxy groups and absorbing electron clouds of the phenyl groups of the addition-curable liquid silicone rubber chains through the boron atoms.

This feature makes borosiloxane oligomers a superior candidate to improve the adhesion and reduce the dislodgement or the exfoliation of the silicone rubber or other materials possessing electron-rich groups on the molecular chains from epoxy resin (59).

1.3.2 Acrylo-Polyhedral Oligomeric Silsesquioxane

Acrylo POSS, a liquid POSS derivative with a reactive C=C double bond, was used to modify addition-cured LSR as an effective nanofiller (60).

Significant enhancements on mechanical properties were obtained. With the addition of only 1.5 *phr* of acrylo POSS to fumed silica-strengthened silicones, the Young's modulus and ultimate tensile strength are increased by 432% and 66%, respectively, and the hardness of resulting LSR composites was improved. NMR and FTIR spectroscopy proved an efficient hydrosilylation between acrylo POSS and hydrosiloxane directly.

The thermal stability and morphology investigations also confirmed that POSS is covalently incorporated into the network of the silicone rubber. The increment of crosslink density was proved by extraction and swelling experiments and dynamic mechanical analysis. It could be envisioned that this simple and effective method could help to produce high performance silicone rubber composites (60).

1.3.3 Cellulose Nanocomposites

To prepare LSR/cellulose nanocrystal nanocomposite, 3-aminopropyltriethoxysilane was used to modify the surface of the cellulose nanocrystal to improve the interfacial interaction between the hydrophilic cellulose nanocrystal and the hydrophobic LSR (61).

FTIR spectroscopy and energy dispersive spectrometry results demonstrated that 3-aminopropyltriethoxysilane modified the cellulose nanocrystal successfully. It was found that a small amount of modified cellulose nanocrystal had better reinforcement than SiO_2 in LSR nanocomposites; the tensile strength and the strain at break of LSR increased over 85% and 44% by adding 1.5% modified cellulose nanocrystal.

However, DSC and rheology tests indicated that 3-aminopropyltriethoxysilane modified cellulose nanocrystals increased the curing temperature of LSR and limited the addition of a cellulose nanocrystal, which was attributed to poisoning of the platinum catalyst by 3-aminopropyltriethoxysilane. Furthermore, a small amount of modified cellulose nanocrystal improved the thermal stability of LSR; the TGA results showed that the 10% weight loss temperature of LSR increased 56°C with a 1.0% addition of modified cellulose nanocrystals (61).

1.3.4 Fluorine-Containing Poly(phenylsilsesquioxane)

It is of great interest to simultaneously improve the anti-pollution and tracking resistance of a silicone rubber for its application in outdoor high voltage insulation (62).

An efficient approach was proposed to address this issue by incorporating fluorine-containing poly(phenylsilsesquioxane) and an ureido-containing MQ (M= $(CH_3)_3SiO$, Q= SiO_4) silicone resin (U-MQ) into addition-cure LSR. The fluorine-containing poly(phenylsilsesquioxane)/U-MQ composition significantly improved the tracking resistance and hydrophobicity of the addition-cure LSR. By adding 2 *phr* fluorine-containing poly(phenylsilsesquioxane) and 1 *phr* U-MQ, addition-cure LSR passed the 1A 4.5 level inclined plane test with merely 0.2% eroded mass, and had a water contact angle as high as 121 Å. The synergism of fluorine-containing poly(phenylsilsesquioxane) and U-MQ on suppressing the addition-cure LSR degradation was further revealed and demonstrated. These findings exhibited great potential for fabricating silicone rubber with prominent tracking and erosion resistance by the combination of prevention and inhibition of tracking damage, endowing it with excellent long-term stable service performance (62).

1.3.5 Silicone Rubber Overmolded Poly(carbonate)s

Poly(carbonate)s (PCs) and blends of PC and polyester are utilized in a wide variety of molded structures, for instance, automotive parts, medical devices, medical device components, electronic device components such as cell phones, glasses, and goggles, such as virtual reality googles and safety goggles.

These materials are forming structures that have rigid surfaces. Rigid surfaces can be irritating to users. To reduce or prevent structures formed from PCs from irritating users, softer materials such as cured silicon rubbers are overmolded onto the surfaces or a portion of the surfaces of such structures.

However, cured silicon rubbers do not bond well to the surfaces of molded PCs (63). A number of references disclose methods of enhancing the bonding of silicon rubber in the cured state to PCs (64–66).

The market demands cost-effective solutions that further enhance the bond strength of silicon rubber to molded PCs (63).

Articles have been published which include the following solutions (63): A molded substrate consisting of one or more PC resins or blends of PC and polyester resins containing poly(dimethyl siloxane)s modified with acrylate groups, hydroxyl groups, or epoxy groups. These are disposed on the surface. Or a portion of the substrate is a cured silicone rubber; PCs contain the modified poly(dimethyl siloxane)s in a sufficient amount, such that the peel strength of the cured silicone rubber from the molded substrates after curing is enhanced.

A number of test plaques were prepared for testing the PC compositions. The test plaques were molded using the following conditions (63):

The compositions were blended in a twin screw extruder at 260°C and injected into a mold of the size 5 *cm*× 5 *cm* × 0.3 *cm* for unfilled resins and 5 *cm* × 5 *cm* × 2.0 *cm* for fiber-reinforced resins. The blend was injected at 300°C, with an injection speed of 200 $mm\,s^{-1}$ and an injection pressure of 2500 $kp\,cm^{-2}$. The residence time in the mold was about 40 *s*. Then, the plaques were removed and cooled.

Afterwards a liquid silicone rubber composition containing an alkenyl group-containing organopolysiloxane, an organohydrogenpolysiloxane having at least two hydrogen atoms each directly attached to a silicon atom in a molecule, an addition reaction catalyst, selected from platinum and platinum compounds, was applied to one surface of the plaques in a strip of 2 *cm* wide, 4 *cm* long and having a thickness of 0.4 *mm* for plaques without glass fibers and 2.0 *mm* for plaques with glass fiber.

The plaques with the applied silicone rubber composition were cured, cooled and a peel test was done according to ASTM D3330 (67).

The addition of a modifier to the PC improves the peel force by about 30% or greater. The articles exhibit an excellent bonding strength between the substrate PCs that contain the modified poly(dimethyl siloxane)s. The peel strength of the cured silicone rubber from an unfilled substrate after curing at 115°C for 5 *min* may be about 1.80 $kg\,mm^{-1}$ or greater; the substrate has a thickness of 0.3 *mm* (63).

1.3.6 Urethane-Containing Silane

Rapid crosslinking of silicone chains on the nanosilica surface during arc discharge has been proposed as an efficient strategy to improve the tracking and erosion resistance of silicone rubber (68).

Urethane-containing silane was synthesized from (3-isocyanatopropyl)triethoxysilane, isopropyl alcohol and allyl alcohol via nucleophilic addition and transetherification (68). The synthesis is shown in Figure 1.19.

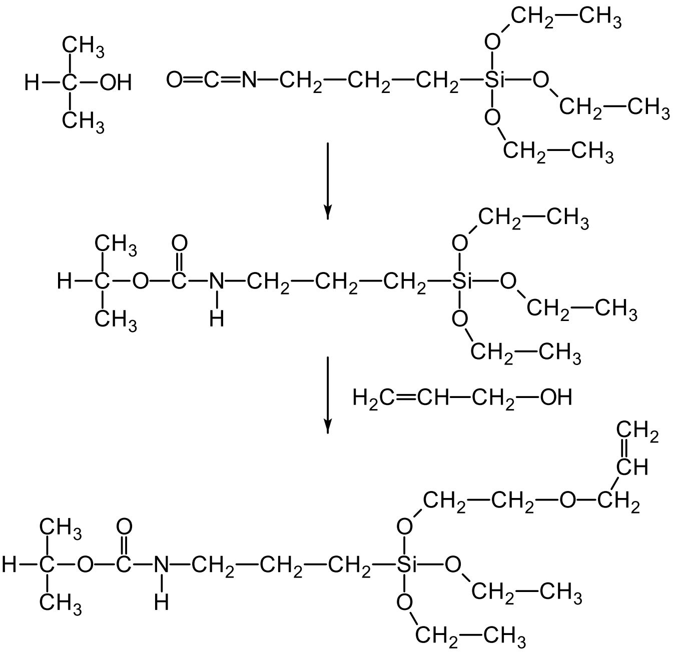


Figure 1.19 Synthesis of urethane-containing silane (68).

The suppression effect and mechanism of urethane-containing silane on the tracking and erosion of addition-cure liquid silicone rubber/silica nanocomposite were investigated.

It was found that urethane-containing silane could significantly enhance the tracking and erosion resistance of addition-cure liquid silicone rubber/silica. When only 2.5 *phr* urethane-containing silane was added, all the addition-cure liquid silicone rubber/silica/urethane-containing silane specimens passed the inclined plane test at 4.5 *kV* and the erosion rate decreased from 3.44% to 0.25%.

This might occur, because urethane-containing silane tightly constrained silicone chains on the silica surface by strong hydrogen-bonding interactions. During the arc discharge, urethane-containing silane at the interphase enhanced the catalytic activity of platinum compound to promote the radical crosslinking of silicone chains absorbed on the silica surface.

Hence, a compact and intact ceramic layer was quickly formed on the addition-cure liquid silicone rubber surface and protected the underlying materials from further arc ablation. These results provide a new method and theoretical basis for the design, preparation and application of the novel high-performance polymer insulating material (68).

1.3.6.1 Thermal Stability

A reactive urea-containing silane, (γ-diethylureidopropyl)allyloxyethoxysilane, was synthesized by a transetherification reaction (69). The synthesis is shown in Figure 1.20. The chemical structure was characterized by FTIR and ^{1}H NMR.

The silane was incorporated into addition-cure liquid silicone rubber using a hydrosilylation reaction. The thermal stability of the addition-cure liquid silicone rubber samples was investigated by TG and TG-FTIR.

When the urea-containing silane was incorporated, the temperature of 10% weight loss and 20% weight loss under air atmosphere were increased by 31°C and 60°C in comparison to those of the addition-cure liquid silicone rubber without the urea-containing silane. In addition, the residual weight at 800°C increased from 33.5% to 58.7%.

It was concluded that the enhancement in the thermal stability of the addition-cure liquid silicone rubber samples could be attributed to the decomposition of the urea groups to isocyanic acid, which reacted with hydroxyl groups to inhibit the unzipping depolymerization (69).

1.3.7 Glass Fiber Fabric

High silica glass fiber fabric/liquid silicone rubber composite sheets filled with hollow glass microspheres were prepared (70). The effects of the hollow glass microspheres content on the mechanical, thermal

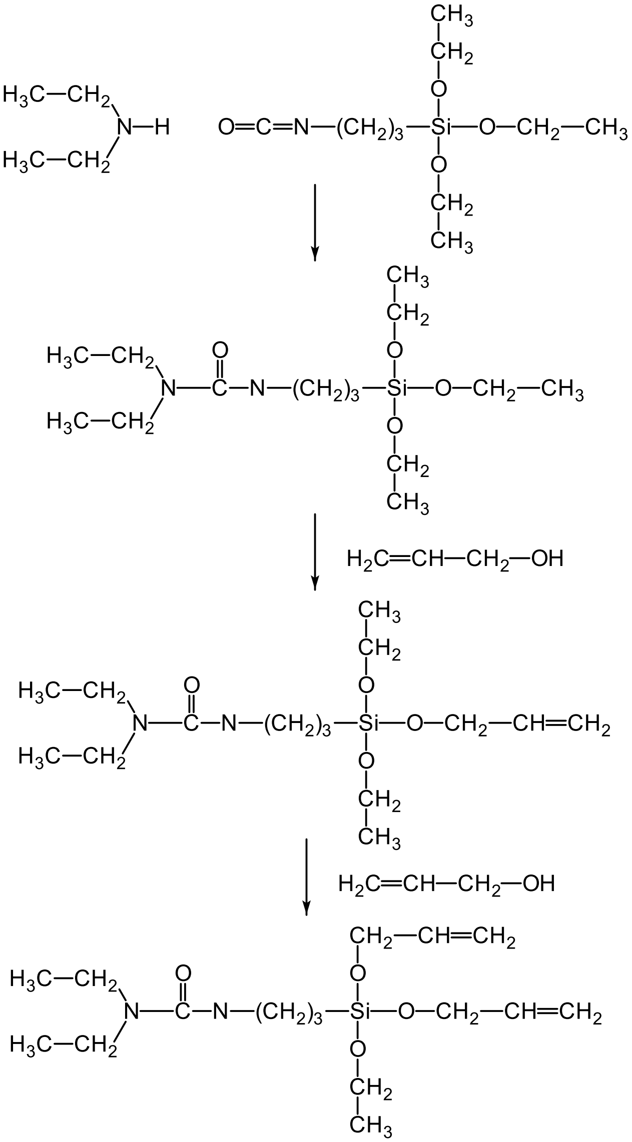


Figure 1.20 Synthesis of (γ-diethylureidopropyl)allyloxyethoxysilane (69).

insulation, and the dynamic mechanical properties of the composite sheets were investigated.

The results showed that the compatibility and interfacial properties between the hollow glass microspheres and the matrix were improved when the hollow glass microspheres were treated with a silane coupling agent, KH550. This is a 3-aminopropyltriethoxysilane coupling agent, c.f. Figure 1.21.

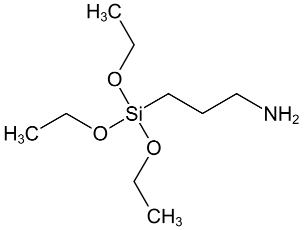


Figure 1.21 3-Aminopropyltriethoxysilane.

A composite in which the hollow glass microspheres' content was 7% by weight, showed the most advantageous mechanical, insulating and damping properties (70).

1.3.8 Foams

1.3.8.1 Cellular Foams

An overview of manufacturing processes used in the development of cellular silicone for a wide variety of applications has been given (71).

The combination of the intrinsic properties of silicone and a foam is considered an attractive solution for many applications. Foaming is very common in hydrosilylation/condensation reactions. This well-known technology leads to homogeneous, elastic, low density and biocompatible foams. However, if the size of the cells remains large, the reactions are sensitive to humidity and the dangerousness of the hydrogen could be an industrial concern. Alternatives for the manufacture of silicone cellular materials are gas foaming, phase separation, emulsion and sacrificial models, and syntactic charges.

In addition, the theories of sorption, diffusion, nucleation and cell growth were detailed to explain the formation of gaseous foam (71).

CO_2 is commonly used to physically foam silicone because of its good solubility. However, the diffusive behavior of CO_2 is high in silicone, as explained by the free volume theory. Silicone-CO_2 foaming is essentially triggered by rapid depressurization, leading to a cell density of around 1×10^9 cells per cm^3 in the best case. Templated foams can be subdivided into emulsion polymerization foams, sacrificial foams, and syntactic foams. These methods are simple because they do not need specific foaming equipment. Also, the pore sizes are tunable as a function of the template sizes (71).

1.3.8.2 Microcellular Crosslinked Silicone Rubber Foams

A series of microcellular silicone rubber/silica/POSS foams were prepared using supercritical carbon dioxide (72).

The effect of the POSS particles on the rheological behavior, vulcanizing, and cellular morphology of the composites was investigated. The results showed that the POSS grafted carboxylic acid group can improve the matrix strength of silicone rubber. POSS grafted carboxylic acid group act as inhibiting agent in the vulcanizing process.

POSS particles play an important role in the microcellular structure formation. When the POSS content was 2.0%, the cell size and cell density can reach 3.77 μm and 7.99×10^9 cells per cm^3, respectively (72).

Influence of Reinforcing Agent on Cellular Morphology. A series of microcellular silicone rubber foams were prepared using supercritical carbon dioxide (73).

A methylvinyl silicone rubber and fumed silica were used. The hydrophobic silica was modified by the hexamethyldisilazane, c.f. Figure 1.22. Dicumyl peroxide was used for vulcanizing. In the compositions, 10 parts of methylvinyl silicone rubber, 6 parts of hydroxy silicone oil, and 1 part of dicumyl peroxide were used, whereas the amount of silica varied from 40 to 70 parts.

The effect of silica as reinforcing agent on the rheological behavior, cellular morphology and nucleation of silicone rubber composites was investigated.

The results indicated that the silica not only acts as reinforcing agent but also plays an important role in the cellular nucleation.

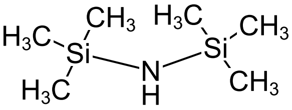


Figure 1.22 Hexamethyldisilazane.

When the content of silica increases from 40 *phr* to 70 *phr*, the range of the calculated surface tension of the silicon rubber composites and the radius of the critical nucleus are 158.95 $nN\,m^{-1}$ to 1,092.74 $nN\,m^{-1}$ and 14.45 *nm* to 99.34 *nm*, respectively.

The aggregated silica shows a good heterogeneous nucleation as the diameter of aggregated silica particles becomes approximate twice. The smallest cell diameter and the highest cell density of the silicone rubber foam can reach 708 *nm* and 1.02×10^{11} cells/cm^3, which indicates that the silicone rubber nanofoams can be obtained by means of the supercritical foaming technology (73).

1.3.9 Addition Type Liquid Phenyl Silicone Rubber

A phenyl silicone resin reinforced addition type liquid phenyl silicone rubber was prepared by the vulcanization of vinyl end-capped poly(methylphenyl siloxane), phenyl MT (74) resins, and hydrogen end-capped poly(diphenyl siloxane) under Pt catalysis at 150°C for 4 *h* (75). The effects of the proportion and the vinyl content of phenyl MT resins on the mechanical properties of cured products were investigated. The vulcanizing mechanism of the phenyl silicone rubber with tetraethoxysilane is shown in Figure 1.23.

The thermal stability was explored by TGA. The changes in mechanical properties were also studied before and after irradiation. A phenyl silicone rubber with good performance was obtained when the phenyl MT resin content was 50% to 60% and the vinyl content was at 5.5% to 6.6 wt%. The onset temperature of thermal degradation and the center temperature of thermal degradation were 443.7°C and 502°C, respectively.

When the radiation dose increased from 0 to 300 *KGy*, the tensile strength decreased from 4.1 *MPa* to 2.3 *MPa* and the tearing strength

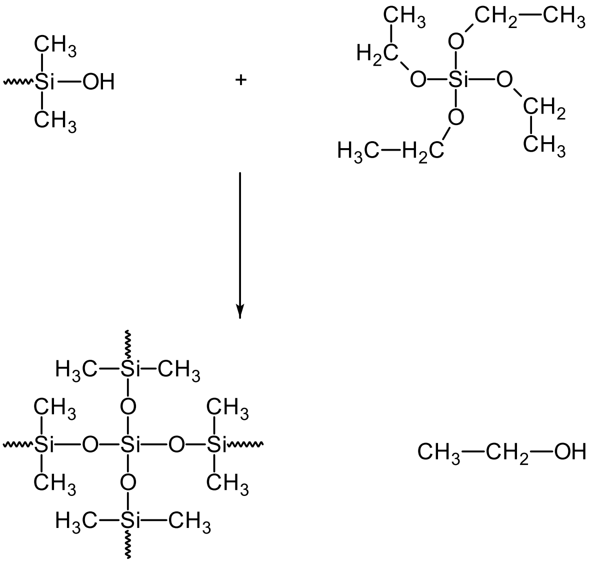


Figure 1.23 Vulcanizing mechanism of phenyl silicone rubber (75).

decreased from 8.9 *MPa* to 5.1 *MPa*. When the radiation dose continued to increase from 300 to 900 *KGy*, the tensile strength increased from 2.3 *MPa* to 6.4 *MPa* and the tearing strength increased from 5.1 *MPa* to 6.5 *MPa*. During the process of radiation, the elongation at break had been kept down from 96% to 52% (75).

A thermal degradation mechanism of room temperature vulcanized phenyl silicone rubber that was vulcanized with different crosslinking agents has been discussed (76).

Room temperature vulcanized phenyl silicone rubber samples were prepared by curing hydroxyl-terminated poly(methyldiphenyl siloxane) via three crosslinking agents, namely, tetraethoxysilane, tetrapropoxysilane, and polysilazane, c.f. Figure 1.24.

The ablation properties of room temperature vulcanized phenyl silicone rubber were studied by the muffle roaster test and FTIR. Then, the thermal stability of the three samples was studied by TG analysis.

In order to explore the thermal degradation mechanism, the room temperature vulcanized phenyl silicone rubber vulcanized by different crosslinking agents was characterized by thermogravimetric

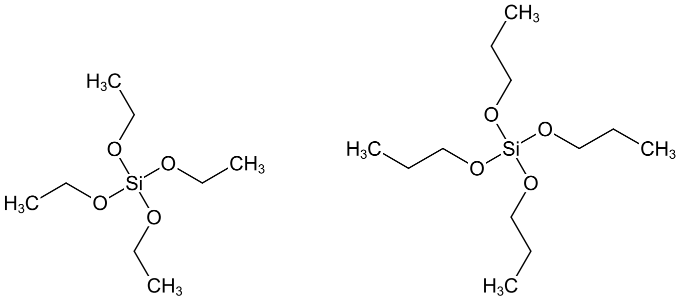


Figure 1.24 Crosslinking agents.

analysis-mass spectrometry (TG-MS) and pyrolysis-gas chromatography mass spectrometry (Py-GC-MS).

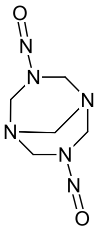
The thermal stability of room temperature vulcanized phenyl silicone rubber is related to the amount of the residual Si–OH groups. The residual Si–OH groups initiated the polysiloxane chain degradation via an unzipping mechanism (76).

1.3.10 Organic Foaming Agent

The silicone rubber foam can basically be obtained by compounding an organic foaming agent such as 2,2′-azobisisobutyronitrile, azodicarbonamide, dinitrosopentamethylenetetramine, c.f. Figure 1.25, and a curing agent into a thermosetting millable silicone rubber composition, and then foaming and curing the resultant silicone rubber composition by heating. In order to obtain a silicone rubber foam having excellent characteristics, it is necessary to balance the foaming rate (decomposition rate) of the organic foaming agent and the curing rate of the silicone rubber composition.

If the decomposition rate of the organic foaming agent is lower than the curing rate of the silicone rubber composition, cells become fine but the foaming ratio becomes low, whereas if the curing rate of the silicone rubber composition is lower than the decomposition rate of the organic foaming agent, gas generated by decomposition of the organic foaming agent cannot be sufficiently captured, resulting in a low foaming ratio and an uneven cell structure.

2,2′-Azobisisobutyronitrile Azodicarbonamide



Dinitrosopentamethylenetetramine

Figure 1.25 Organic foaming agents.

In addition, since the organic foaming agent has a high decomposition rate and rapidly generates gas, it is necessary to bring the silicone rubber composition into a predetermined crosslinked state at a time when the organic foaming agent decomposes in order to capture the generated gas.

In crosslinking by peroxide, the crosslinking rate can be adjusted to a certain degree by selection of an organic peroxide and a compounding amount, but it is difficult to strictly adjust the crosslinking density at a time of decomposition of the organic foaming agent, thus resulting in the disadvantage of requiring the compounding of an excessive amount of organic foaming agent or strictly managing process conditions.

A composition for silicone rubber foam may contain:

1. 100 parts by mass of alkenyl group-containing poly(organo siloxane) with a degree of polymerization of 4,000 to 10,000,
2. An amount of poly(organo hydrogen siloxane) having an average of two or more hydrogen atoms bonded to a silicon atom in a molecule so that a molar ratio of the sili-

con-atom-bonded hydrogen atoms to the alkenyl groups in the component 1 is 0.001 to 5,

3. 0.1 to 10 parts by mass of an organic foaming agent with a decomposition temperature of 50–250°C,
4. 5 to 200 parts by mass of silica powder, and
5. A catalyst amount of a platinum-based metal compound catalyst activated with ultraviolet rays.

A manufacturing method of a silicone rubber foam includes (77):

1. Irradiating the composition for silicone rubber foam with ultraviolet rays at a temperature lower than the decomposition temperature of the organic foaming agent to obtain a crosslinked body, and
2. Heat-treating the crosslinked body at a temperature equal to or higher than the decomposition temperature of the organic foaming agent to obtain a silicone rubber foam.

1.3.11 Foams without Chemical Blowing Agents

Various methods can be used to prepare foamed polymers (78). Some methods involve the use of a physical or chemical blowing agent. Physical blowing agents are generally volatile liquids that can be used to create voids in a matrix, thereby producing a cellular or foamed material.

Common physical blowing agents include chlorofluorocarbons, hydrochlorofluorocarbons, hydrocarbons and liquid carbon dioxide. Chemical blowing agents expand the foam using one or more chemical reactions that produce a gas. An exemplary chemical blowing agent is powdered titanium hydride, which can be used to make metallic foams by decomposing into titanium and hydrogen gas at elevated temperatures. Other foaming methods include mechanical frothing, extraction of soluble fillers, and use of hollow sphere and/or porous particles (78).

Silicone materials in general have low thermal conductivity, low chemical reactivity, low toxicity, good oxidation stability and good thermal stability. These properties make them particularly useful in thermoacoustic, electrical insulation, and sealing applications that demand high temperature resistance, low smoke generation, and/or high biocompatibility.

One of the potential disadvantages of using blowing agents, frothing, fillers, and hollow or porous particles to create voids in a foam is the potential introduction of impurities into the foam material. This can be problematic in applications where such impurities might cause an adverse chemical or biological reaction. Another limitation faced by some of these methods is the lack of independence between the steps of foaming of the material and the polymerization of the foam material. If these processes occur simultaneously, it can be technically challenging to obtain a desirable cell size and/or obtain a suitable distribution of cell sizes.

It was discovered that a silicone precursor derived from tetraalkoxysilane (Q unit) and trimethylethoxysilane (M unit), known as *MQ resin*, can effectively absorb a significant amount of water to obtain a stable MQ-water cluster. Because the water can be subsequently removed by vaporization, this MQ-water cluster can act as a blowing agent to provide foamed silicone structures. The steps of preparation run as follows (78):

1. Disperse water into the MQ resin to form a stabile cluster.
2. Disperse the MQ-water cluster into the silicone fluid to get an inverted emulsion.
3. Polymerize the silicone emulsion.
4. Foam the emulsion by removing the water.
5. Get the final product.

A micrograph of the produced silicone foam is shown in Figure 1.26.

This micrograph shows the open cells. The cells are separated by polymeric struts. Depending on the relative amount of water dispersed in the MQ-water cluster and the relative amount of MQ-water cluster dispersed in the silicone emulsion, it is possible to tailor the thickness of the polymeric struts. The geometry of the struts can influence mechanical characteristics of the overall foam, including, for example, strength, friability, and pressure required to achieve a compression deflection of 25% (78).

1.3.12 Epoxy-Silicone Copolymer

The introduction of an epoxy resin into a liquid silicone rubber not only improves adhesion strength but also the mechanical properties

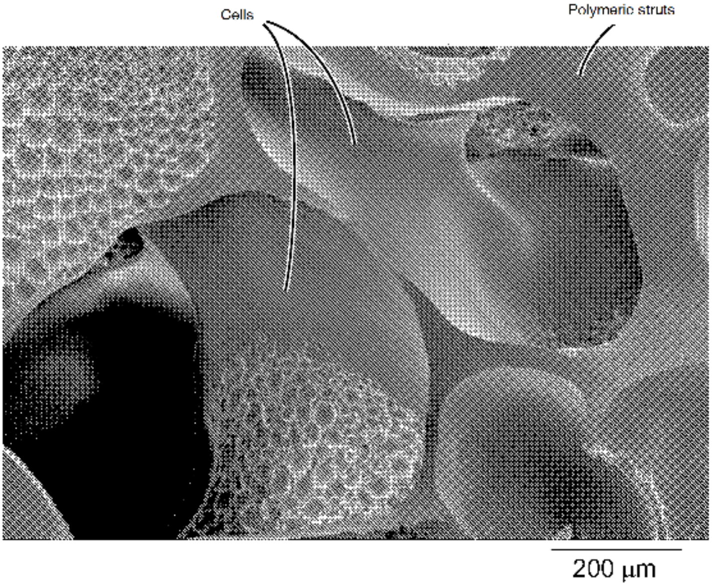


Figure 1.26 Micrograph of the silicone foam (78).

of the silicone rubber (79).

Two different prepolymers were obtained through an efficient hydrosilylation reaction by the changing reaction time and the catalyst dosage in the presence of poly(oxyethylene) epoxy resin and a hydrogen silicone oil with phenyl groups. The reaction is shown in Figure 1.27.

The chemical structure of the prepolymers was confirmed by FTIR ^{1}H-NMR. Then the prepolymers were incorporated into phenyl-containing silicone rubber at different mass fractions. SEM observations demonstrated that a *sea-island* phase separation occurred in the cured composites.

TGA revealed that the thermal stability of silicone rubber composites improved markedly after modification, the residual yield at 800°C achieved 32.69% in the air atmosphere when 20 *phr* hydrogen silicone oil with phenyl groups were introduced.

The studies of the mechanical properties showed that the tensile strength and the shear strength of composites increased gradually with increasing prepolymers.

These results provide very valuable information for understand-

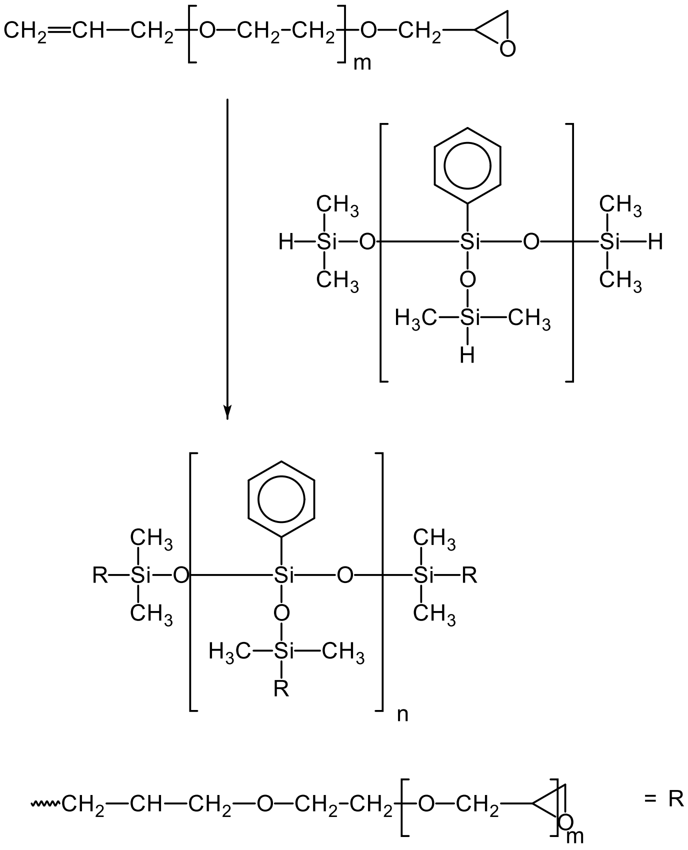


Figure 1.27 Hydrosilylation reaction (79).

ing the hydrosilylation reaction and the effects of the molecular structures on the performance of silicone rubber systems (79).

1.3.12.1 Silicone Defoamer

Many petroleum refineries utilize a delayed coking unit to process the residual oils (80). In a delayed coking, overhead vapors from the coking drum pass through a fractionator where various fractions are separated. One of the fractions is a gasoline boiling range stream.

This stream, commonly referred to as coker gasoline or coker naphtha, is generally a relatively low octane stream, not suitable for use as an automotive fuel without upgrading. With the limitations on octane-enhancing additives imposed by environmental concerns, it has become desirable to process coker gasoline naphtha in an octane-enhancing unit such as a catalytic reformer. Sulfur compounds in coker gasoline are detrimental to catalytic reforming catalysts, and accordingly it has become commonplace to treat coker gasoline in a catalytic desulfurizer prior to processing it in a catalytic reformer. These steps of delayed coking, desulfurization and reforming are well-developed commercial processes which are widely used in the refining industry. Hydrodesulfurization (HDS) catalysts can be undesirably poisoned by silicon. Silicon can also be the poison reforming catalyst, which is even more expensive.

In the delayed coking process, quantities of foam are often produced which are undesirable, as the foam diminishes the efficiency of the delayed coking process. It is customary to add silicone defoamers, such as poly(dimethyl siloxane)s, to delayed cokers to control the undesirable foaming (81). Thus, one of the recurring concerns in the coker is contamination of the products with silicon species that can eventually poison a hydrotreater catalyst and cause the expensive catalyst to be replaced prematurely.

Since the silicone-based defoamer used in the coke drum is believed to be a major source of the silicon contamination, considerable effort has been expended to minimize or eliminate the use of silicone oil from the unit (80). The silicone oil acts both as a defoamer to knock down foam in the drum when the silicone oil is first injected and also acts as an antifoam agent to prevent the subsequent build up of foam. Due to silicone oil's unique surface properties and thermal stability, there has not yet been a commercially viable non-silicone defoamer replacement.

It has been found that crosslinked PDMS resins are useful defoamers and antifoamers for hydrocarbon-containing liquids, such as delayed coker feedstocks and feedstocks to preflash and atmospheric towers (80).

These PDMS resins are crosslinked with either an alkyl poly(silicate) or siloxane. The crosslinked PDMS resins may be used alone or together with linear PDMS, and are typically blended with a carrier such as kerosene for easier handling. Importantly, the use of crosslinked branched PDMS resins permit less total amount of poly(siloxane)s to be used, which reduces the silicon carryover in coker products and reduces poisoning of downstream catalysts (80).

References

1. K.E. Polmanteer, *Rubber Chemistry and Technology*, Vol. 61, p. 470, 1988.
2. J. Ackermann and V. Damrath, *Chemie in unserer Zeit*, Vol. 23, p. 86, 1989.
3. A.F. Jacobine and S.T. Nakos, Photopolymerizable silicone monomers, oligomers, and resins in S.P. Pappas, ed., *Radiation Curing: Science and Technology*, pp. 181–240. Springer US, Boston, MA, 1992.
4. R.B. Allen, P. Kochs, and G. Chandra, Industrial organosilicone materials, their environmental entry and their predicted fate in G. Chandra, ed., *Organosilicon Materials*, Vol. 3H of *The Handbook of Environmental Chemistry*, chapter 1, pp. 1–26. Springer, Berlin New York, 1997.
5. D.E. Katsoulis, R.G. Schmidt, and G.A. Zank, Siloxanes and silicones (advances in silicone technologies 2000-15) in V.Y. Lee, ed., *Organosilicon Compounds*, chapter 7, pp. 301–322. Academic Press, 2017.
6. V. Lee, ed., *Organosilicon Compounds*, Academic Press, London, 2017.
7. M.T. Nazir, B.T. Phung, S. Yu, and S. Li, *IEEE Transactions on Dielectrics and Electrical Insulation*, Vol. 25, p. 2076, Dec 2018.
8. IEC, Electrical insulating materials used under severe ambient conditions – test methods for evaluating resistance to tracking and erosion, IEC 60587, International Electrotechnical Commission, Geneva, Switzerland, 2007.
9. N. Yan, Z. Jia, and X. Zou, *IEEE Transactions on Dielectrics and Electrical Insulation*, Vol. 25, p. 162, February 2018.
10. IEC, Dry, solid insulating materials – resistance test to high-voltage, low-current arc discharges, IEC 61621, International Electrotechnical Commission, Geneva, Switzerland, 1997.

11. S. Ansorge, F. Schmuck, and K.O. Papailiou, *IEEE Transactions on Dielectrics and Electrical Insulation*, Vol. 22, p. 979, April 2015.
12. C. Geng, Q. Zhang, W. Lei, F. Yu, and A. Lu, *Journal of Applied Polymer Science*, Vol. 134, p. 45544, 2017.
13. B.M. Maher, J. Rezaali, K. Jalili, and F. Abbasi, *Rubber Chemistry and Technology*, Vol. 90, p. 108, 2017.
14. H. Ghaleh, K. Jalili, B.M. Maher, R. Rahbarghazi, M. Mehrjoo, S. Bonakdar, and F. Abbasi, *European Polymer Journal*, Vol. 106, p. 305 , 2018.
15. D. Blanc, C. Maliverney, and R. Ferhat, Article having antifouling properties and intended to be used in aquatic applications, particularly marine applications, US Patent Application 20 110 305 911, assigned to Bluestar Silicones France, Lyon Cedex (FR), December 15, 2011.
16. A. Milne, Anti-fouling marine compositions, US Patent 4 025 693, assigned to The International Paint Co., Ltd. (London, ENG), May 24, 1977.
17. A. Acton, ed., *Siloxanes – Advances in Research and Applcation*, p. 95. Scholary Editions, Atlanta, Georgia, 2013.
18. B.M. Maher, J. Rezaali, H. Ghaleh, S. Fallahnejad, F. Abbasi, and A.A. Babaluo, *Colloid and Polymer Science*, Vol. 295, p. 1595, September 2017.
19. C. Baumgart, D. Weiß, and V. Altstädt, *Polymer Engineering & Science*, Vol. 56, p. 849, 2016.
20. H. Sirin, M. Kodal, B. Karaagac, and G. Ozkoc, *Composites Part B: Engineering*, Vol. 98, p. 370, 2016.
21. V. Seitz, K. Arzt, S. Mahnel, C. Rapp, S. Schwaminger, M. Hoffstetter, and E. Wintermantel, *International Journal of Adhesion and Adhesives*, Vol. 66, p. 65, 2016.
22. M. Shimakawa, Silicone rubber composition, method of producing the same, and silicone rubber extrudate, US Patent Application 20 180 291 160, assigned to Momentive Performance Materials Japan LLC, Tokyo (JP), October 11, 2018.
23. K. Han, G. Jo, and B. Kim, Silicone composition and a pressure sensitive adhesive film having a pressure sensitive adhesive layer made from the composition, US Patent Application 20 170 233 612, assigned to Dow Silicones Corp., August 17, 2017.
24. S. Aoki and A. Yamamoto, Silicone composition and a pressure sensitive adhesive film having a pressure sensitive adhesive layer made from the composition, US Patent 8 057 909, assigned to Shin-Etsu Chemical Co., Ltd. (Tokyo, JP), November 15, 2011.
25. T. Morita, Y. Nimura, R. Yamaoka, S. Fukagawa, and T. Seki, Silicone rubber composition and silicone rubber crosslinked body, US

Patent Application 20 180 208 767, assigned to Sumitomo Riko Company Limited, Komaki-shi (JP) and SumiRiko Fine Elastomer, Ltd., Ageo-shi (JP), July 26, 2018.

26. W. Chen, X. Zeng, X. Lai, H. Li, W. Fang, and T. Liu, *Thermochimica Acta*, Vol. 632, p. 1, 2016.
27. S. Azechi, Y. Taira, and T. Yoshida, Addition curing type liquid silicone rubber compositions, US Patent 6 331 588, assigned to Shin-Etsu Chemical Co., Ltd. (Tokyo, JP), December 18, 2001.
28. M. Scholz and J. Meyer, Silicone rubber, US Patent 9 708 458, assigned to Evonik Degussa GmbH (Essen, DE), July 18, 2017.
29. ASTM Subcommittee, Standard test method for silica-*n*-dibutyl phthalate absorption number, ASTM D6854, ASTM International, West Conshohocken PA, 2003.
30. ASTM Subcommittee D24.11, Standard test method for carbon black--oil absorption number of compressed sample (COAN), ASTM D3493, ASTM International, West Conshohocken PA, 2018.
31. H.Y. Jin, Y.F. Li, S.C. Nie, P. Zhang, N.K. Gao, and W. Li, *Materiali in Tehnologije*, Vol. 51, p. 783, 2017.
32. Y. Li, H. Jin, S. Nie, C. Tong, and N. Gao, *AIP Advances*, Vol. 8, p. 015313, 2018.
33. Y. Li, H. Jin, S. Nie, P. Zhang, and N. Gao, *Applied Physics Letters*, Vol. 110, p. 201602, 2017.
34. J. Song, C. Chen, and Y. Zhang, *Composites Part A: Applied Science and Manufacturing*, Vol. 105, p. 1, 2018.
35. J. Wang, D. Zhao, X. Zou, L. Mao, and L. Shi, *Journal of Materials Science: Materials in Electronics*, Vol. 28, p. 12984, 2017.
36. Y. Xue, X. Li, H. Wang, F. Zhao, D. Zhang, and Y. Chen, *Materials & Design*, Vol. 165, p. 107580, 2019.
37. A. Lendlein, ed., *Shape-Memory Polymers*, number 226 in Advances in Polymer Science, Springer, Heidelberg, New York, 2010.
38. J. Leng and S. Du, eds., *Shape-Memory Polymers and Multifunctional Composites*, CRC Press, Boca Raton, FL, 2010.
39. M. Pantoja, Z. Lin, M. Cakmak, and K.A. Cavicchi, *Journal of Polymer Science Part B: Polymer Physics*, Vol. 56, p. 673, 2018.
40. Y. Guo, *Investigation of Silicone Rubber Blends and their Shape Memory Properties*. PhD thesis, University of Akron, Akron, Ohio, 2018.
41. J. Hu, ed., *Advances in Shape Memory Polymers*, number 146 in Woodhead Publishing Series in Textiles, Woodhead Publishing, Cambridge, UK, 2013.
42. Q. Meng, J. Hu, Y. Zhu, J. Lu, and Y. Liu, *Journal of Applied Polymer Science*, Vol. 106, p. 2515, 2007.
43. L. Xu, Thermoplastic elastomer compounds exhibiting shape memory via thermo-mechanical action, US Patent 9 290 652, assigned to PolyOne Corporation (Avon Lake, OH), March 22, 2016.

44. K. Tsuji, K. Yamada, H. Kizaki, and N. Matsumoto, Thermally conductive silicone grease composition, US Patent 9 321 950, assigned to Shin-Etsu Chemical Co., Ltd. (Tokyo, JP), April 26, 2016.
45. X. Luo and D.D.L. Chung, *Journal of Intelligent Material Systems and Structures*, Vol. 8, p. 389, 1997.
46. N.A. Kotov, *Nature*, Vol. 442, p. 254, July 2006.
47. A. Yu, P. Ramesh, M.E. Itkis, E. Bekyarova, and R.C. Haddon, *The Journal of Physical Chemistry C*, Vol. 111, p. 7565, 2007.
48. V. Causin, C. Marega, A. Marigo, G. Ferrara, and A. Ferraro, *European Polymer Journal*, Vol. 42, p. 3153, 2006.
49. S. Ganguli, A.K. Roy, and D.P. Anderson, *Carbon*, Vol. 46, p. 806, 2008.
50. S. Bittolo Bon and L. Valentini, *arXiv preprint*, Vol. 8, 2015.
51. Y. Zhang, X. Zeng, X. Lai, and H. Li, *RSC Advances*, Vol. 8, p. 111, 2018.
52. UL LLC, Standard for tests for flammability of plastic materials for parts in devices and appliances, Online, electronic: https://standardscatalog.ul.com/standards/en/standard_94_6 UL 94, Underwriters Laboratories of the United States, Northbrook, Illinois, 2015.
53. P. Rybiński, B. Syrek, D. Bradło, and W. Żukowski, *Materials*, Vol. 11, p. 1298, 2018.
54. L.A. Bloomfield, *arXiv preprint arXiv:1801.09253*, Vol. 1, p. 1, 2018.
55. W. Noll, ed., *Chemistry and Technology of Silicones*, Academic Press, Oxford, 1968.
56. R.W. Boot, Process for preparing organo-polysiloxane compositions, US Patent 3 213 048, assigned to General Electric, October 19, 1965.
57. L.A. Bloomfield, Viscoelastic silicon rubber compositions, US Patent 9 550 864, assigned to University of Virginia Patent Foundation (Charlottesville, VA), January 24, 2017.
58. S. Rubinsztajn, *Journal of Inorganic and Organometallic Polymers and Materials*, Vol. 24, p. 1092, November 2014.
59. X. Zhao, C. Zang, Y. Sun, K. Liu, Y. Wen, and Q. Jiao, *Journal of Materials Science*, Vol. 53, p. 1167, January 2018.
60. J. Sun, J. Kong, and C. He, *Journal of Applied Polymer Science*, Vol. 136, p. 46996, 2019.
61. X. Li, Q. Wu, M. Zheng, Q. Li, S. Wang, and C. Zhang, *Cellulose*, Vol. 25, p. 473, January 2018.
62. T. Wu, X. Lai, F. Liu, H. Li, and X. Zeng, *Applied Surface Science*, Vol. 459, p. 483, 2018.
63. K.-l.L. Cheng, C.W. Hung, C.T. van Nuffel, and C.-W.W. Chang, Molded structures of polycarbonate based substrates over molded with silicone rubbers, US Patent Application 20 190 031 916, assigned to Trinseo Europe GmbH, January 31, 2019.

64. H. Fujiki, S. Shudo, A. Matsuda, N. Ogawa, and T. Takata, Polycarbonate resin/silicone rubber integrally molded article and method for making, US Patent 5 366 805, assigned to Shin-Etsu Chemical Company, Ltd. (Tokyo, JP), November 22, 1994.
65. H. Fujiki and S. Shudo, Thermoplastic resin compositions for use in integral molding with silicone rubber and integrally molded parts, US Patent 5 792 812, assigned to Shin-Etsu Chemical Co., Ltd. (Tokyo, JP), August 11, 1998.
66. H. Fujiki and S. Shudo, Thermoplastic resin compositions for use in integral molding with silicone rubber and integrally molded parts, EP Patent 0 722 990, assigned to Shin-Etsu Chemical Co. Ltd., February 12, 1997.
67. ASTM Subcommittee D10.14, Standard test method for peel adhesion of pressure-sensitive tape, ASTM D3330, ASTM International, West Conshohocken PA, 2018.
68. Y. Zhang, X. Zeng, X. Lai, H. Li, and X. Huang, *Polymer Testing*, Vol. 69, p. 16, 2018.
69. W. Fang, X. Zeng, X. Lai, H. Li, W. Chen, and Y. Zhang, *Thermochimica Acta*, Vol. 605, p. 28, 2015.
70. S. Chen, Y. Qin, J. Song, and B. Wang, *Polimery*, Vol. 63, 2018.
71. T. Métivier and P. Cassagnau, *Journal of Cellular Plastics*, Vol. 55, p. 151, 2019.
72. T. Liu, Y. Lei, F. Zhang, S. Guo, and S. Luo, *Polymer-Plastics Technology and Engineering*, Vol. 57, p. 1623, 2018.
73. B. Xiang, Z. Deng, F. Zhang, N. Wen, Y. Lei, T. Liu, and S. Luo, *Polymer Engineering & Science*, Vol. 59, p. 5, 2019.
74. The Dow Chemical Company, Fascinating silicones, Online, electronic: https://consumer.dow.com/en-us/fascinating-silicones.html, Dow Chemical Company, Midland (Michigan), USA, 2018.
75. D. Peng, Q.H. Mu, S. Zhang, J.H. Li, and F. Wang, Synthesis and properties of phenyl silicone resin reinforced addition type liquid phenyl silicone rubber, in *International Symposium on Advanced Material Research II*, Vol. 926 of *Materials Science Forum*, pp. 39–44. Trans Tech Publications, August 2018.
76. C. He, B. Li, Y. Ren, W. Lu, Y. Zeng, W. He, and A. Feng, *Materials*, Vol. 12, p. 88, December 2018.
77. M. Shimakawa, Composition for silicone rubber foam, manufacturing method of silicone rubber foam, and silicone rubber foam, US Patent 9 340 655, assigned to Momentive Performance Materials Japan LLC (Tokyo, JP), May 17, 2016.
78. J.J. Liu, P. Wu, F. Bai, and D.A. Ylitalo, Silicone compositions and related methods, US Patent 9 540 494, assigned to 3M Innovative Properties Company (Saint Paul, MN), January 10, 2017.

79. B. Zhang, R. Li, J. Luo, Y. Chen, H. Zou, and M. Liang, *Polymer Bulletin*, Vol. 75, p. 2105, May 2018.
80. L.N. Kremer, Silicone defoamer to better control hydrocarbon foam and reduce silicon content of liquid hydrocarbon products, US Patent 7 427 350, assigned to Baker Hughes Incorporated (Houston, TX), September 23, 2008.
81. J.A. Hyde, Silicone oil antifoam, US Patent 3 700 587, assigned to Nalco Company LLC, October 24, 1972.