Reactive Silicones

by D. Wewers

Introduction

Reactive silicones is a general heading which represents a multitude of totally different structures describing the various functional silicones, e.g. RTV (room temperature vulcanizing) or HTV (high temperature vulcanizing) rubbers. Silicone resins, those products with high cross linkage, also belong to the group of reactive silicones. I shall restrict my lecture exclusively to linear organofunctional polysiloxanes in which the reactive organic group is bonded to silicone via a hydrocarbon bridge.

From this group of linear organofunctional siloxanes, the strictly difunctional α,ω-organo-functional siloxanes have experienced, in recent years, a continually growing academic and economic interest as reactive modification reagents for the synthesis of organic polymers. Examples of such organofunctional siloxanes are hydroxy-, amino-, epoxy-, carboxy- or acryloxyalkyl-functional polydimethylsiloxanes. From this point of view, the lecture is organized as follows: first, I shall speak about the starting siloxanes that are necessary for synthesis of organofunctional siloxanes. Then, I shall discuss the production of a few selected α,ω-organofunctional siloxanes. Finally, I shall demonstrate the application of these siloxanes as soft segments in ABA and $(AB)_n$ block copolymers.

Structures of Organofunctional Siloxanes

Organofunctional siloxanes, i.e., compounds in which a functional group is bonded to silicon by a silicon-carbon bond, can be synthesized from siloxanes that contain silicon-hydrogen groups by addition of organic compounds with terminal double bonds (Fig. 1). This kind of reaction is called hydrosilylation [1].

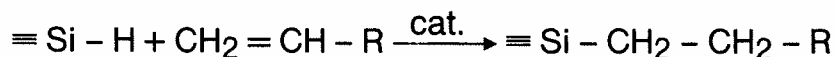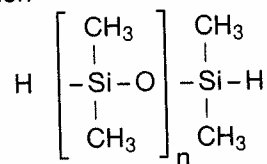$$\equiv Si - H + CH_2 = CH - R \xrightarrow{\text{cat.}} \equiv Si - CH_2 - CH_2 - R$$
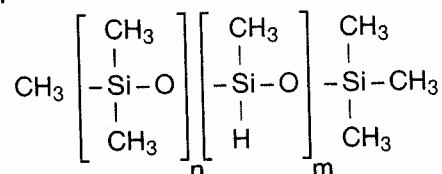
Fig. 1: Hydrosilylation reaction

In those siloxanes that are important for these reactions, the Si-H groups can be situated at various locations in the linear molecule (Fig. 2). They can be in terminal, in side or in terminal and side positions.

If organic groups are reacted with SiH-groups in the side position, comb-like structures are obtained. If the organic groups are added at the ends, α,ω-difunctional silicones are obtained. In the case of additions to the terminal and side positions, then logically a combined comb-like and α,ω-modified siloxane is obtained.

terminal position

$$H \left[\begin{array}{c} CH_3 \\ | \\ -Si-O \\ | \\ CH_3 \end{array} \right]_n \begin{array}{c} CH_3 \\ | \\ -Si-H \\ | \\ CH_3 \end{array}$$

side position

$$CH_3 \left[\begin{array}{c} CH_3 \\ | \\ -Si-O \\ | \\ CH_3 \end{array} \right] \left[\begin{array}{c} CH_3 \\ | \\ -Si-O \\ | \\ H \end{array} \right]_m \begin{array}{c} CH_3 \\ | \\ -Si-CH_3 \\ | \\ CH_3 \end{array}$$

terminal- and side position

$$H \left[\begin{array}{c} CH_3 \\ | \\ -Si-O \\ | \\ CH_3 \end{array} \right]_n \left[\begin{array}{c} CH_3 \\ | \\ -Si-O \\ | \\ H \end{array} \right]_m \begin{array}{c} CH_3 \\ | \\ -Si-H \\ | \\ CH_3 \end{array}$$
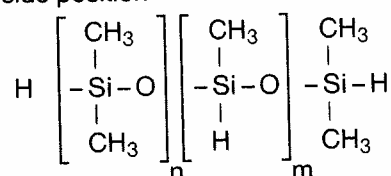
Fig. 2: Polysiloxanes with Si-H groups

Production of SiH-functional Siloxanes

As already mentioned, the hydrogen siloxanes play a decisive role in the synthesis of organofunctional siloxanes. This leads to the question: how are siloxanes and especially hydrogen siloxanes produced?

Starting products for the synthesis of methylsiloxane are methylchlorosilanes which are manufactured on a large scale from silicon and methyl chloride by the Rochow or the direct synthesis. The main product of the Rochow synthesis is dimethyldichlorosilane [2] with a yield between 85 and 88%. In second place is methyltrichlorosilane with a yield between 6 and 15%. Compared to the dimethyldichlorosilane the synthetically important hydrogen containing silanes are generated only in minor amounts.

The monomethyldichlorosilane (MeHSiCl$_2$) from which the hydrogen siloxane with SiH-groups in the side position, shown in Fig. 2, is produced by cohydrolysis with dimethyldichlorosilane (Me$_2$SiCl$_2$) and trimethylmonochlorosilane (Me$_3$SiCl); it is isolated normally with a yield of only 2%. The dimethylmonochlorosilane (Me$_2$HSiCl) makes up 20–30% of the low-boiling fraction which itself represents only 0.5% of the total amount of the silanes produced by the Rochow-Synthesis; it must be separated by extensive fractional distillation.

Several methods of synthesis can be used to produce α,ω-bishydridopolydimethyl-siloxanes from the dimethylmonochlorosilane. One possibility is to hydrolyse the pure silane to tetramethyldisiloxane which, subsequently, is equilibrated with dimethyl-
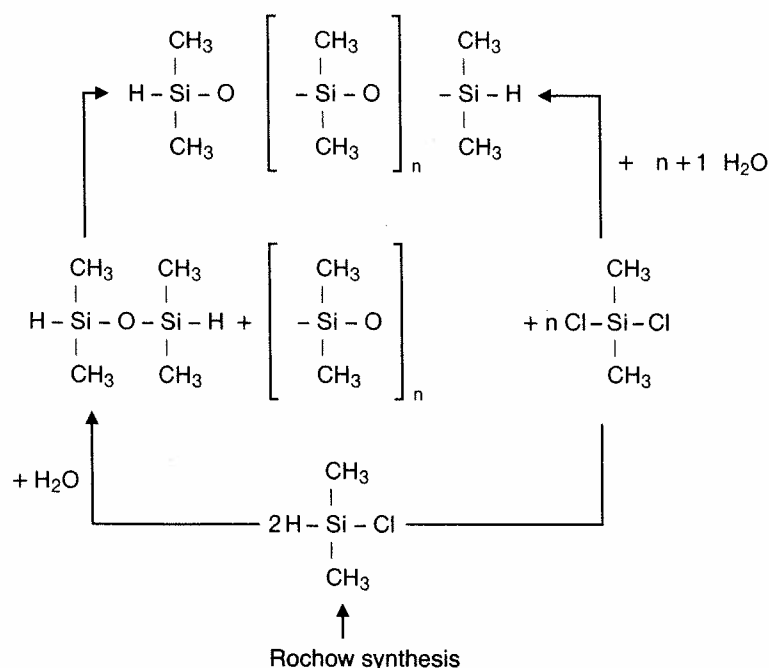
Fig. 3: Reaction path for the synthesis of α,ω-bishydrido polydimethylsiloxanes

siloxanes. In this manner, one obtains linear hydrogen siloxanes with a higher molecular weight. Alternatively, one can also carry out a cohydrolysis of dimethyldichlorosilane and dimethylmonochlorosilane. This leads directly to the higher-molecular hydrogen siloxanes. These synthesis procedures are used by the Bayer AG and Wacker-Chemie GmbH companies.

Other Production Methods for a α,ω-functional Hydrogen Siloxanes

The current availability of these α,ω-hydrogen siloxanes by way of direct synthesis is not unlimited. With increasing interest in α,ω-organofunctional siloxanes the interest in the availability of such α,ω-bishydridopolydimethylsiloxanes also increases. Proof of this is the extensive literature on processes for the manufacture of such hydrogen siloxanes. Most frequently described is the reduction of halogen silanes or siloxanes to the corresponding hydrogen compounds. For example, a process is described [3] in which lithium aluminium hydride reacts with chlorosiloxane (Fig. 4). However, in this reaction, the siloxane chain is partly decomposed. A split-off product of this decomposition is dimethylsilane (Me_2SiH_2), a highly flammable gas. A further drawback is the aqueous processing of the reaction product. For this reason, the Th. Goldschmidt AG has developed a new process [4] with the aim of transforming the α,ω-dihalogen polydimethylsiloxanes into the corresponding hydrogen siloxanes by reaction with metal hydrides without chain decomposition. At the same time, the process should be guaranteed to be harmless.
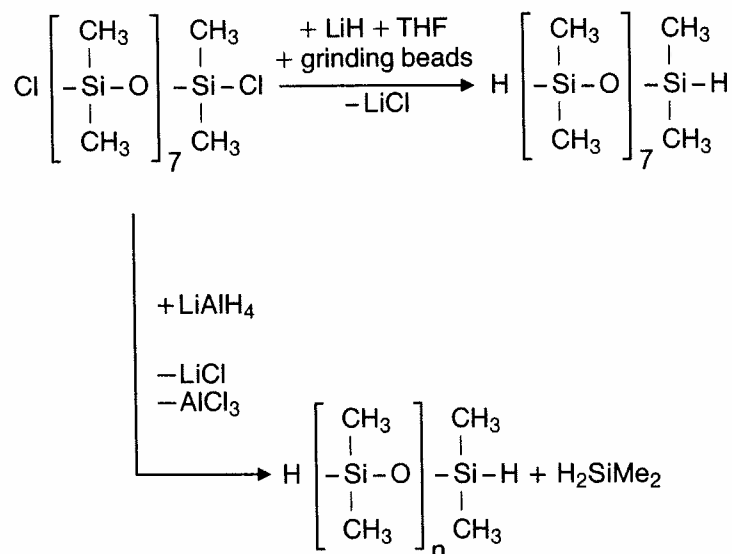
$$Cl\left[-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{Si}}-O\right]_7 \underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{Si}}-Cl \xrightarrow[-LiCl]{\substack{+\ LiH\ +\ THF \\ +\ grinding\ beads}} H\left[-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{Si}}-O\right]_7 \underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{Si}}-H$$

$$+ LiAlH_4$$
$$- LiCl$$
$$- AlCl_3$$

$$\longrightarrow H\left[-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{Si}}-O\right]_n \underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{Si}}-H + H_2SiMe_2$$

Fig. 4: Representation of α,ω-bishydrido polydimethylsiloxanes

In this process, a dichloro polydimethylsiloxane reacts with lithium hydride in the presence of tetrahydrofurane. The lithium chloride formed, which is difficult to dissolve in THF, is deposited on the surface of the lithium hydride which is then deactivated. To prevent this, the reaction must proceed in the presence of grinding beads. Under these conditions, the lithium hydride always remains active and it becomes possible to transform the chlorosiloxane completely into hydrogen siloxane. The lithium chloride formed during the reaction can be separated without any difficulty. This synthesis makes it possible to have unlimited amounts of α,ω-hydrogen siloxanes.

Production of Organofunctional Siloxanes

As mentioned at the beginning, compounds with terminal double bonds can be attached to siloxanes that contain silicon-hydrogen groups. The α-olefines, vinyl- or allyl-compounds are here of technical interest. These addition reactions can be catalyzed, for example, by UV radiation or peroxides. Addition then proceeds according to a mechanism involving radicals.

Technically speaking, the use of transition-metal catalysts these normally are complexes of platinum or rhodium is considerably more interesting because there are fewer byproducts. Most authors, who have studied transition-metal catalysis, start with a coordination mechanism. Chalk and Harrod [5] formulated the following mechanism for hexachloroplatinum acid: The process begins with the reduction of platinum at an oxidation level of +4 to platinum at oxidation level +2. This platinum is then coordinated with the olefin whereby the actual catalyst is formed. In the third step, the $\equiv$ Si-H is added to the catalyst by oxidation. In the fourth step, the π-bonded olefin is inserted into the platinum-hydrogen compound forming a σ-complex. According to Chalk and Harrod, this is a decisive step. The final step is the reductive elimination of the end
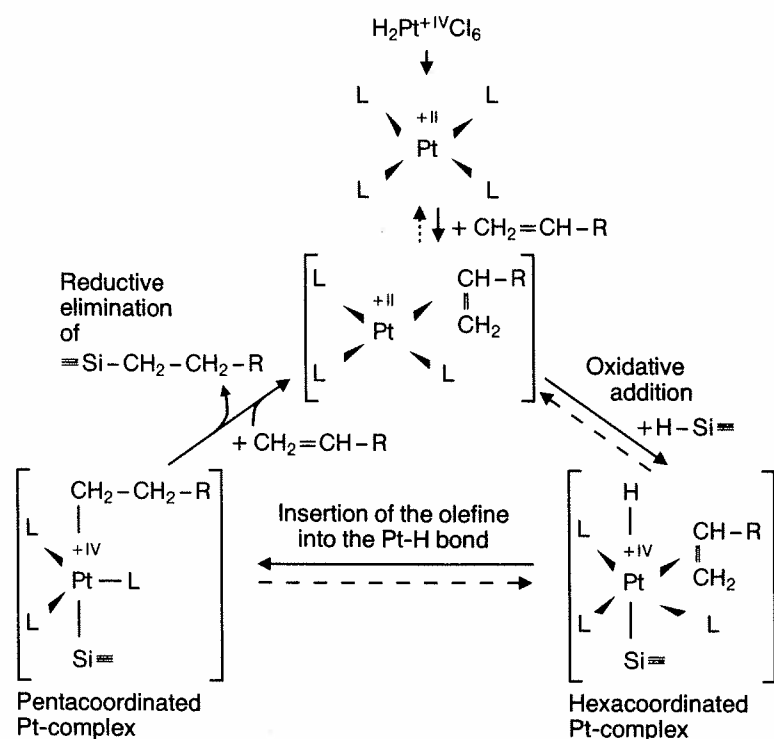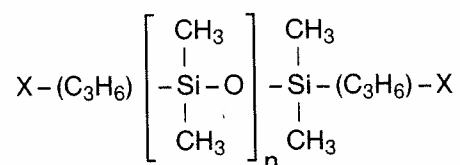
$$H_2Pt^{+IV}Cl_6$$

Fig. 5: Reaction mechanism of a hydrosilylation reaction

product. At the same time, the catalyst is regenerated by addition of the olefin, and the reaction cycle can start anew. Only a few ppm of catalyst are required for these reactions. Several organofunctional siloxanes produced by transition metal catalysis are shown in Fig. 6. It is remarkable, that in all examples the linear basic structure is the same. Only the reaction group X changes; X can be a hydroxy-, an amino-, an epoxy-, an acrylate- or a carboxy-radical. Other radicals have also been introduced.

Production of α,ω-organofunctional Siloxanes

In principle, the production methods for comb-like and α,ω-functional siloxanes are comparable. For both groups, the reaction conditions for the hydrosilylation reaction must be adjusted for the functional group that is to be introduced. I should like to illustrate more closely the problems that occur with hydrosilylation of the siloxanes for the example shown in Fig. 6.

$$X-(C_3H_6)\left[\begin{array}{c}CH_3\\|\\-Si-O\\|\\CH_3\end{array}\right]_n\begin{array}{c}CH_3\\|\\-Si-(C_3H_6)-X\\|\\CH_3\end{array}$$

X = Hydroxy $-OH$

X = Amino $-NH_2$

X = Epoxy $-O-CH_2-\overset{\displaystyle O}{\overset{/\backslash}{CH}}-CH_2$

X = Acrylat $-O-CH_2-\underset{\underset{OH}{|}}{CH}-CH_2-O-\underset{\underset{O}{\|}}{C}-CH{=}CH_2$

X = Carboxy $-O-\underset{\underset{O}{\|}}{C}-CH_2-CH_2-\underset{\underset{O}{\|}}{C}-OH$

Fig. 6: Functional siloxanes

Hydroxyfunctional Polydimethylsiloxanes

As shown in Fig. 7, the starting products for hydroxyfunctional siloxanes are α,ω-SiH-functional siloxanes and allyl alcohol. Although direct addition of allyl alcohol to hydrogen siloxanes is described in the patent literature [6], it is technically hardly realizable. The reaction between the hydridic hydrogen of the siloxane and the acidic hydrogen of the alcohol under release of hydrogen is an inconvenient competing reaction during the process: one encounters, among others, allyloxysiloxanes which are unstable during the hydrolysis and which again are starting products for further secondary reactions. Hydrogen developed during formation of allyloxysiloxanes does not escape completely but is partly used up for reduction of allyloxysiloxane to propoxysiloxane. At the same time, the double bond of allyloxysiloxane reacts partly by hydrosilylation with the hydrogen siloxane. A further secondary reaction is the β-addition of the allyl alcohol. The resulting products are thermally unstable and decompose into propene and siloxanol which, for example, can condense under acidic conditions with a release of water. Propene is partially bonded to the hydrogen siloxane and leads to propylsiloxanes. Because of this secondary reaction, more complicated reaction paths are selected for the synthesis. In most cases the allyl alcohol is provided with a protective group (e.g., acetate, trimethylsilyl) [7] and this protected alcohol is added to the siloxane. The protective group is subsequently removed. Even these seemingly simple reactions are not without problems.

A ^{1}H-NMR spectrum of a pure hydroxypropyl-modified siloxane is shown in Fig. 8. The signal at $\delta = 0$ ppm corresponds to the methyl groups of the siloxane chain. The multiplets at $\delta = 3.6$ ppm can be correlated with the three methyl groups of the propylene radical.
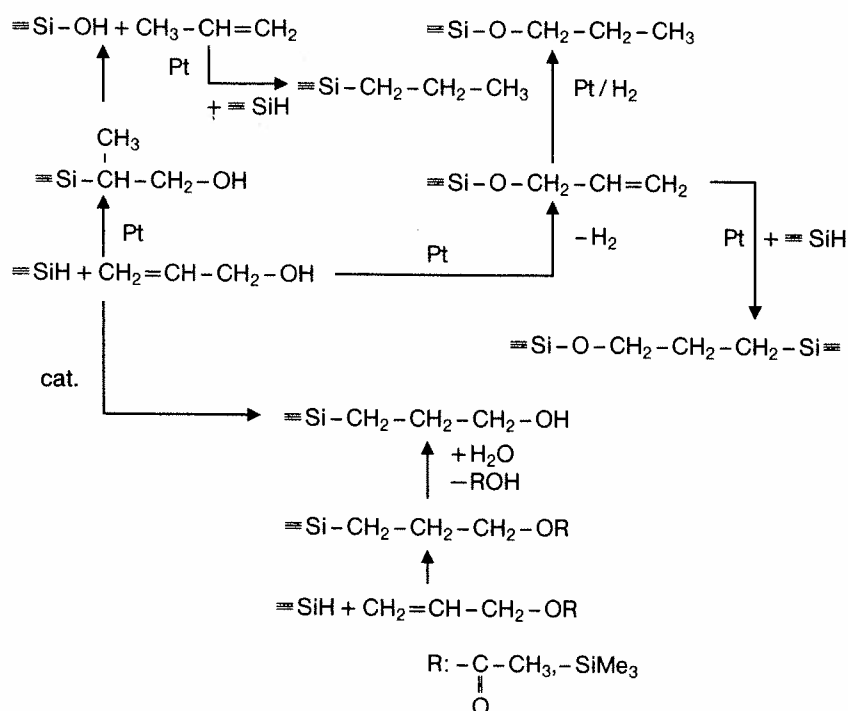
$$\equiv Si-OH + CH_3-CH=CH_2 \qquad \equiv Si-O-CH_2-CH_2-CH_3$$

$$\xrightarrow[+\ \equiv SiH]{Pt} \equiv Si-CH_2-CH_2-CH_3 \quad \Big| Pt/H_2$$

$$\begin{array}{c} CH_3 \\ | \\ \equiv Si-CH-CH_2-OH \end{array} \qquad \equiv Si-O-CH_2-CH=CH_2 \xrightarrow{\qquad}$$

$$\Big\uparrow Pt \qquad\qquad \xrightarrow{Pt} \quad \Big\uparrow -H_2 \qquad Pt \Big| +\equiv SiH$$

$$\equiv SiH + CH_2=CH-CH_2-OH \xrightarrow{\qquad}$$

$$\equiv Si-O-CH_2-CH_2-CH_2-Si\equiv$$

cat.

$$\equiv Si-CH_2-CH_2-CH_2-OH$$

$$\Big\uparrow \begin{array}{c} +H_2O \\ -ROH \end{array}$$

$$\equiv Si-CH_2-CH_2-CH_2-OR$$

$$\Big\uparrow$$

$$\equiv SiH + CH_2=CH-CH_2-OR$$

$$R: \begin{array}{c} -C-CH_3, -SiMe_3 \\ \| \\ O \end{array}$$

Fig. 7: Addition of allyl alcohol

The proton of the hydroxyl group has a resonance frequency at 3.9 ppm. From the ratio of the methylene protons of the propylene radical to the methyl groups of the siloxane, one can compute the average chain length, that is, the average molecular weight. One obtains an average chain length of 8.6 Si units for the shown α,ω-bis(hydroxypropyl) polydimethylsiloxane; this corresponds to an average molecular weight of 738 g/mol.

An entirely different path may be used to synthesize 1,3-bis(4-hydroxybutyl) tetramethyl-disiloxane (Fig. 9). Here, tetrahydrofuran reacts with dimethyldichlorosilane and magnesium in boiling tetrahydrofuran. This is a special reaction which is based on the high formation tendency of the six membered ring and therefore cannot be generalized. The generated 2,2-dimethyl-1-oxa-2-silacyclohexane is dissolved in water with a small amount of hydrochloric acid and forms the hydroxyfunctional siloxane with a yield of about 70 %.

Aminofunctional Polydimethyl Siloxanes

The potential danger from the addition of allyl amine is much greater than from the addition of allyl alcohol. By this it is ment not only the danger of secondary reactions as described for allyl alcohol, and the possible deactivation of the hydrosilylation catalyst by allyl amine but much more problematic is the increased susceptibility of SiH-groups to spontaneous uncontrollable reactions. Therefore, it is recommended to use less
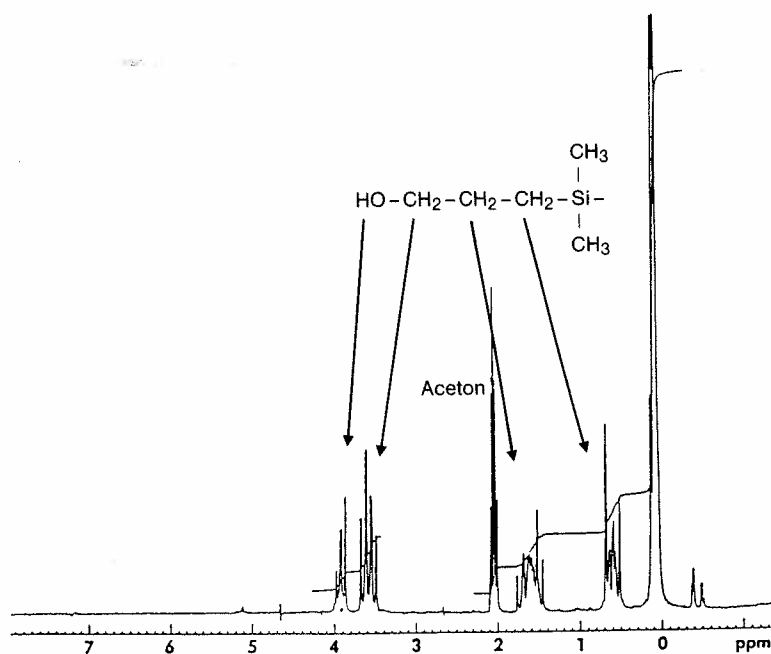
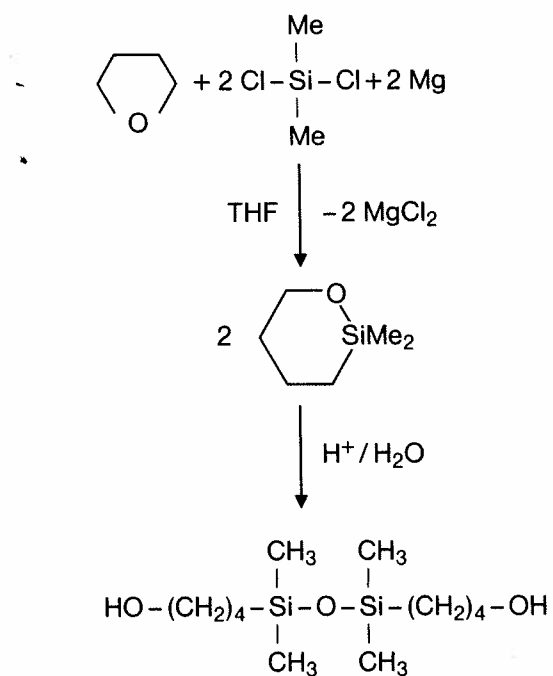Fig. 8: ^{1}H-NMR spectrum of an α,ω-bis(hydroxypropyl) polydimethylsiloxane

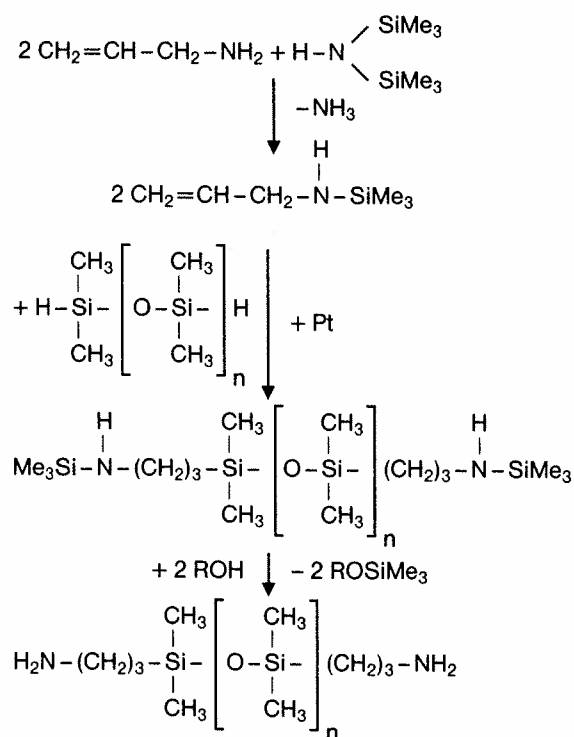Fig. 9: Synthesis of 1,3bis(4-hydroxybutyl)tetramethyldisiloxane

$$2\ CH_2\!=\!CH\!-\!CH_2\!-\!NH_2 + H\!-\!N\!\!\begin{array}{c}\diagup SiMe_3 \\ \diagdown SiMe_3\end{array}$$

$$\downarrow\ -NH_3$$

$$2\ CH_2\!=\!CH\!-\!CH_2\!-\!\underset{|}{\overset{H}{N}}\!-\!SiMe_3$$

$$+\ H\!-\!\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{Si}}\!-\!\left[\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{O\!-\!Si}}\right]_n\!\!H \quad +\ Pt$$

$$\downarrow$$

$$Me_3Si\!-\!\underset{|}{\overset{H}{N}}\!-\!(CH_2)_3\!-\!\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{Si}}\!-\!\left[\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{O\!-\!Si}}\right]_n\!\!(CH_2)_3\!-\!\underset{|}{\overset{H}{N}}\!-\!SiMe_3$$

$$+\ 2\ ROH\ \downarrow\ -\ 2\ ROSiMe_3$$

$$H_2N\!-\!(CH_2)_3\!-\!\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{Si}}\!-\!\left[\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{O\!-\!Si}}\right]_n\!\!(CH_2)_3\!-\!NH_2$$

Fig. 10: Addition of allyl amine

dangerous and also less costly processes. These processes start with an allyl amine that is provided with a protective group [8] (Fig. 10). The protective group is added in the first reaction step. Here, allyl amine reacts with hexamethyldisilazane or with trimethyl-monochlorosilane to form N-trimethylsilylallyl amine. This derivatived allyl amine is then attached to the siloxane by a hydrosilylation reaction. In the last step, the intermediate product is converted to α,ω-bis(aminopropyl) polydimethylsiloxane by alcoholysis.

Epoxyfunctional Polydimethylsiloxanes

Hydrosilylation of allyl glycidyl ether or vinylcyclohexene oxide, to name just two representatives, proceeds largely without problems [9]. At least, no reaction of hydridic hydrogen with the epoxy group has been observed. However, the process requires special attention. Epoxyfunctional polydimethylsiloxanes are superbly suitable as starting materials for further reactions (Fig. 11).

Processing of an epoxyfunctional siloxane with a large excess of piperazine yields a siloxane which is both amino- and hydroxyfunctional.

If the oxirane ring is opened with acrylic or methacrylic acid one obtains acrylate or methacrylate-functional polymethylsiloxanes [9]. Reaction of the oxirane ring with an alcohol or with water, again in large excess, leads to mono- or dihydroxyfunctional siloxanes.
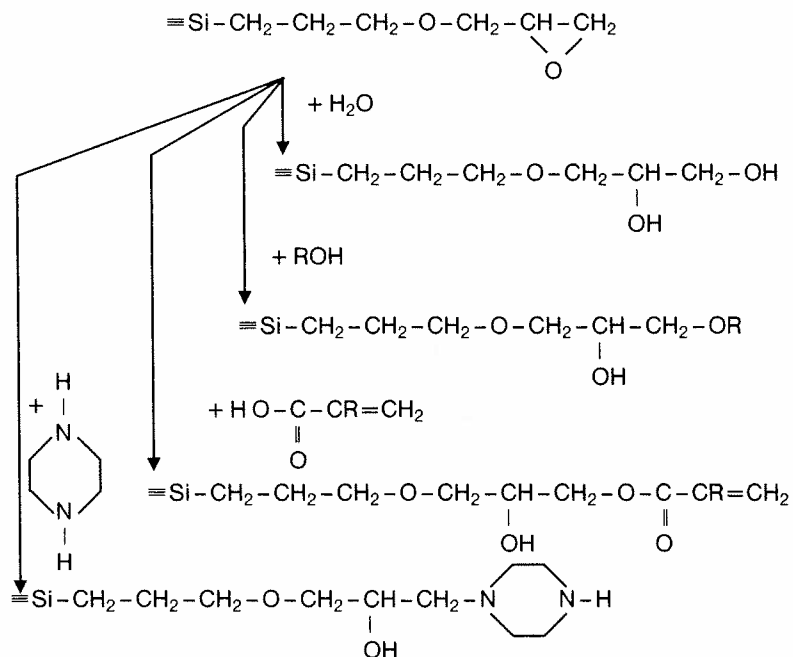
$$\equiv Si-CH_2-CH_2-CH_2-O-CH_2-CH-CH_2$$
$$\underset{O}{\diagdown\diagup}$$

$+ H_2O$

$\equiv Si-CH_2-CH_2-CH_2-O-CH_2-CH-CH_2-OH$
$|$
OH

$+ ROH$

$\equiv Si-CH_2-CH_2-CH_2-O-CH_2-CH-CH_2-OR$
$|$
OH

$$+ HO-\underset{\underset{O}{\|}}{C}-CR=CH_2$$

$\equiv Si-CH_2-CH_2-CH_2-O-CH_2-CH-CH_2-O-\underset{\underset{O}{\|}}{C}-CR=CH_2$
$|$
OH

$\equiv Si-CH_2-CH_2-CH_2-O-CH_2-CH-CH_2-N\quad N-H$
$|$
OH

Fig. 11: Reactions of epoxysiloxanes

α,ω-organofunctional Siloxanes as Soft Segments in ABA or (AB)ₙ Block Copolymers [9]

So far, I have talked about the production of hydrogen and of organofunctional siloxanes. To conclude my lecture I should like to discuss the application of these building blocks as soft segments in ABA or $(AB)_n$ block copolymers. Pure organic ABA or $(AB)_n$ block copolymers frequently consist of phase-separated, hard, glass-like or crystalline segments and soft rubber-like segments. Important representatives of such block copolymers are the two-block copolymers of polystyrol and polybutadiene (SB) or the three-block copolymers of polystyrol, polybutadiene and polystyrol (SBS). The degree of phase separation is affected by compatibility, block length and crystallinity of the individual parts.

A relatively simple method for examining phase separation is the measurement of the glass-transition temperature (Tg). In the case of separate phases, one measures two different glass temperatures which correspond to those of the pure individual phases. If the system consists of a single phase one finds only an intermediate glass-transition temperature.

A measure of the compatibility of two polymers is the difference between their solubility parameters. The experimentally determined solubility parameter of polydimethyl-siloxanes is near $\delta = 7.3-7.5$ $(cal/cm^3)^{1/2}$. The solubility parameter of most organic polymers lies between $\delta = 8.5$ and 14 $(cal/cm^3)^{1/2}$. It is evident from this data that the sometime extreme incompatibility of the siloxanes is the driving force for the formation

of a multi-phase system. If the reactive siloxane replaces, partly or completely, the organic soft segment A then its properties are introduced into the polymer matrix.

In the following, I want to list the "the unique property profile" of polydimethylsiloxanes:

extremely low glass temperatures of $-123\,°C$,
very low surface tension of $20-21$ mN/m,
good thermal stability,
good permeability for gases,
physiological inertness,
good hydrophobicity.

If one considers this profile of properties it becomes understandable why reactive organic siloxanes are so attractive as polymer elements. Their attractiveness is indicated by the steadily rising number of publications which deal with the theme siloxane-modified polymers. Table 1 gives an overview of siloxane-modified polymer systems.

Table 1: Organosilicone Copolymer Systems

Siloxane/Polysulfone Copolymer
Siloxane/Polyurethane Copolymer
Siloxane/Polyurea Copolymer
Siloxane/Polyamide Copolymer
Siloxane/Polyimide Copolymer
Siloxane/Polyamide/Polyimide Copolymer
Siloxane/Polyester Copolymer
Siloxane/Polycarbonate Copolymer
Siloxane/Polystyrene Copolymer
Siloxane/Epoxide Resin Networks

In principle, there are two possibilities to modify organic polymers with reactive organo-functional siloxanes. One possibility is to add the siloxane, at the desired concentration, during the entire synthesis of the base polymer. The other possibility is to produce, by a special reaction, a siloxane-modified polymer as so-called master batch which subsequently is mixed with an unmodified base polymer. In this case one speaks of a polymer-alloy or a polymer-blend.

Siloxane-Polymide Copolymer

The first siloxane-polyimide copolymer was described already by Kuckertz [10] in 1966. Since that time the number of scientific publications and patents [11] has increased rapidly.

Polyimides are of special interest for the electronics and aerospace industries because of their outstanding thermal and mechanical properties. Unfortunately these polymers are mostly insoluble in fully imidized form. By purposeful insertion of flexible siloxane segments into the polyimide matrix, it has become possible to synthesize siloxane-polyimide copolymers that are more soluble, easier to process and exhibit good thermal stability in spite of the modification. Furthermore, this insertion increases atmospheric stability and impact strength. Resistance to water absorption is also improved.
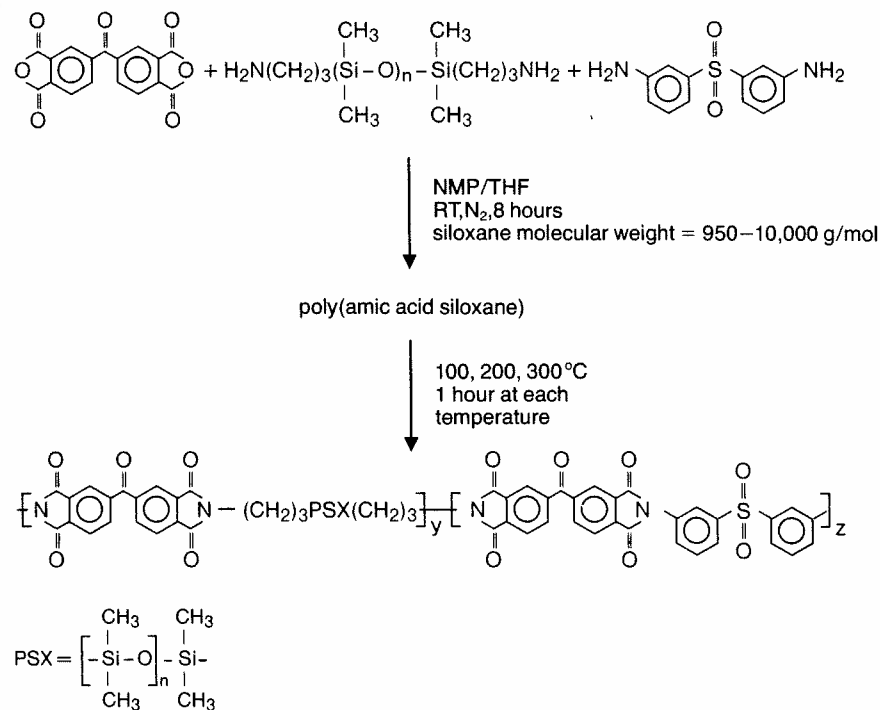
Bott et al.

Fig. 12: Siloxane-polyimide-copolymer

The process of the synthesis is shown in Fig. 12. In the two-step reaction, Bott et al. [11] stirred 3,3,4,4-benzophenonetetracarbonic acid dianhydride, 3,3-diaminodiphenyl-sulfone and various α,ω-bis(aminopropyl) polydimethylsiloxanes for eight hours at room temperature in a solvent mixture of N-methylpyrrolidine (NMP) and tetrahydrofuran (THF). The clear and viscous poly(amic acid siloxane) acid copolymers obtained in this manner were dried in this layers for one hour at 100 °C, 200 °C or 300 °C. For gravimetric tests, an α,ω-bis(aminopropyl) polydimethylsiloxane with a mean molecular weight of 950 g/mol was built into the polyimide at 10, 20, 40 and 60 weight percent according to the method described in the foregoing. An unmodified polyimide served as reference (Fig. 13).

As can be clearly seen from Fig. 13, the thermal stability varies only with the siloxane fraction. While an unmodified polyimide can be heated to 550 °C without decomposition, a polyimide modified up to 60 weight percent with an aminosiloxane decomposes already at 400 °C. The decomposition temperature for a modification of 10 weight percent lies at a still acceptable temperature of 500 °C. In tests in which the degree of modification was kept constant at 10 weight percent aminosiloxane, but the mean molecular weight of the aminosiloxane was varied, the thermal stability increased with increasing molecular weight of the siloxane. These experiments suggest that decomposition of siloxane-polyimide copolymer must begin with the propylene groups which bond the siloxane to the polyimide matrix, because the concentration of the propylene groups decreases for a higher molecular weight of the bis(aminopropyl) polydimethylsiloxane.

siloxane Mn = 950 g/mol
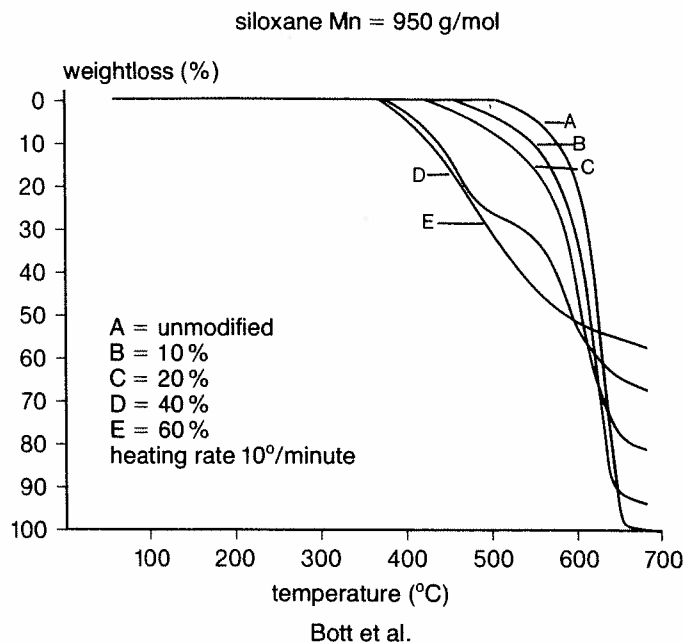
Fig. 13: Thermo-gravimetric analysis of a siloxane-polyimide copolymer

The surface of these siloxane-polyimide copolymers was examined by photoelectron spectroscopy (ESCA). It was found that the siloxane fraction at a depth of 1−2 nm lies near 85−87 weight percent, independent of whether the degree of siloxane modification was 5 or 40 weight percent and the mean molecular weight was 950 g/mol or 10,000 g/mol in the siloxane-polyimide copolymer. On the other hand, already at a depth of 5−7 nm, one can observe a relationship between the degree of siloxane modification in the copolymer and the siloxane fraction on the surface. For a modification degree of 5 weight percent of an aminosiloxane with a mean molecular weight of 950 g/mol, one finds 34 weight percent siloxane at a depth of 5−7 nm. For a modification degree of 40 weight percent, the siloxane fraction at a depth of 5−7 nm rises to 63 weight percent.

One can state in conclusion that siloxane-polyimide copolymers exhibit good thermal properties and that there is siloxane enrichment on the surface. This explains the increased atmospheric stability and the reduced water absorption of siloxane-polyimide copolymers.

Siloxane-Urea Block Copolymers [12]

Yilgör, McGrath et al. have prepared numerous publications on the subject of organo-modified copolymers. They synthesized (AB)$_n$-siloxane-urea copolymers from 4,4-di-phenylmethanediisocyanate (MDI) and α,ω-bis(aminopropyl)polydimethylsiloxanes. They reacted equimolar amounts of aminosiloxane with the isocyanate in such a manner that a solution of the aminosiloxane in glycoldiethyl ether at room temperature dripped into a mixture of MDI, glycoldiethyl ether and dimethylacetamide. Here, the dimethyl-

acetamide acts as a solubilizer between the extremely nonpolar siloxane and the developing block copolymer which contains highly polar urea compounds. After complete addition, the temperature is increased to 50°C for 1 hour to assure complete reaction. The solvent is extracted in a vacuum at 50°C. In this manner, aminosiloxanes with molecular weights of 1100, 1800, 2400 or 3700 g/mol were processed and the modulus of elasticity and the glass-transition temperature were determined (Table 2).

Table 2: Siloxane-Urea Block Copolymers

Product No	Molecular Weight (g/mol)	Chain Length	Modulus of Elasticity (MPa)	Siloxane Fraction (%)	Tg Siloxane Phase (°C)
1	1100	13	33.7	82	−118
2	1800	22	19.1	88	−121
3	2400	30	7.1	91	−121
4	3700	47	5.1	94	−123

As expected, the modulus of elasticity is correlated with the siloxane concentration; it decreases from 33.7 N/mm^2 to 5.1 N/mm^2 if the siloxane fraction is increased from 82% to 94%. The glass transition temperature of a siloxane-urea block copolymer with a siloxane fraction of 82% lies at −118°C. If the siloxane fraction is increased to 92% the glass transition temperature falls to −123°C. This transition temperature is also found for pure polydimethylsiloxanes.

It is clear from the stress-strain diagram that the tensile strength and elongation at break are directly related to the siloxane concentration (Fig. 14). With increasing siloxane content, the tensile strength decreases from about 11 N/mm^2 for a siloxane-urea copolymer with 82% siloxane to about 4 N/mm^2 for a copolymer with 94% siloxane. At the same time, the elongation at break increases with increasing siloxane content. While a copolymer with 82 weight percent of siloxane has an elongation at break of about 600%, a copolymer with 94 weight percent of siloxane exhibits an elongation at break of over 900%.

A further phenomenon that occasionally is observed with thermoplastic block copolymers is shown particularly clearly for product No. 1. One recognizes that the stress-strain curve rises linearly at first and reaches a point where the slope changes because of irreversible deformation of the substance. This point is called yield point. In conclusion, one can thus maintain that such siloxane-urea copolymers exhibit outstanding elastomeric properties.

Siloxane-Epoxide Networks [13]

α,ω-glycidoxypropyl-modified polydimethylsiloxanes are incompatible with the basic resin bisphenol-A-diglycidyl ether (DGEBA) and separate after relatively short storage time of the mixture. We have established that by adding 0.5−1% of a silicone surfactant it is possible to emulsify 10−20% of the epoxyfunctional siloxanes in bisphenol-A-diglycidyl ether in a stable manner. These emulsions can subsequently be cured with trimethylhexamethylene diamine (TMD).

Test	Weight percent	
	siloxane	urea
1	82	18
2	88	12
3	91	9
4	94	6

Yilgör et al.
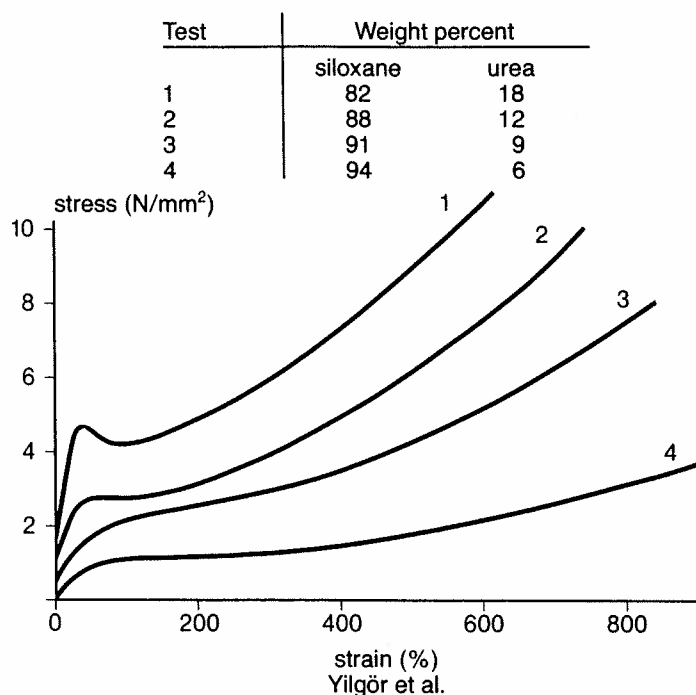
Fig. 14: Stress-strain diagram for siloxane-urea copolymers

The usual curing conditions for amine-cross-linked epoxide systems are keeping these for three days hardening at room temperature and finally for three hours at 105 °C. Films of modified and unmodified epoxide resin 150 μm thick, were produced by this curing method (Table 3).

Tabelle 3: Siloxane-Epoxide Networks

Basic resin (DGEBA)	100 g	90 g	80 g	58 g	36 g
Epoxy-Siloxane (1100 g/mol)	—	10 g	20 g	—	—
Carboxy-Siloxane					
A (1250 g/mol)	—	—	—	42 g	—
B (2370 g/mol)	—	—	—	—	64 g
Silicone surfactant	—	0.6 g	1.2 g	—	—
Hardening Material (TMD)	21.4 g	19.8 g	18.9 g	9.2 g	5.5 g
Tensile Strength (N/mm^2)	38 ± 8	39 ± 3	36 ± 2	16 ± 2	2 ± 0,4
Elongation at break (%)	< 1	3	4.6	25	32
Remark	transparent very brittle	turbid flexible	turbid flexible	transparent flexible	transparent flexible

If 10 or 20 % of the basic resin (DGEBA) are replaced by an epoxyfunctional polydimethyl-siloxane with a mean molecular weight of 1100 g/mol, then the elongation at break increases from less than 1 % to 3 or 4.6 %, respectively. However, the tensile strength is only insignificantly affected; it is of the order of near 40 N/mm^2.

Carboxyfunctional polydimethylsiloxanes produced by reaction of an α,ω-hydroxypropyl-modified polydimethylsiloxane with succinic acid anhydride can also be used to modify epoxy resins. It is possible to produce transparent foils and castings with such modified resins. For this purpose, a prepolymer is produced in a special step from DGEBA and the carboxyfunctional siloxane in the ratio of 4:1. This mol ratio corresponds to a weight ratio of 58 g DGEBA to 42 g siloxane A with a mean molecular weight of 1250 g/mol or 36 g DGEBA to 64 g siloxane B with a mean molecular weight of 2370 g/mol. Again, one uses TMD as hardening agent.

The high proportion of siloxane B has a marked influence on the tensile strength which is reduced from about 40 N/mm^2 for the unmodified epoxy resin to 16 N/mm^2 and 2 N/mm^2 for modification with siloxane A and siloxane B, respectively. The effect of the increased siloxane proportion is remarkable. On the other hand, the elongation at break is clearly increased from less than 1 % to 25 % for siloxane A and 32 % for siloxane B. The influence of the increased siloxane proportion is here far less strongly marked.

These results indicate that relatively small concentrations of an organofunctional siloxane can make the brittle starting material flexible; larger added amounts of certain siloxanes markedly increase the elongation at break, while there is some decrease in the tensile strength.

Summary ~

In my lecture, I have spoken about linear α,ω-organofunctional polydimethylsiloxanes in which the reactive organic group is bonded to the siloxane by a hydrocarbon bridge. They are synthesized by hydrosilylation reactions between polydimethylsiloxanes with silicon-hydrogen groups in terminal positions and compounds with terminal double bonds. The linear hydrogen siloxanes are produced either from the dimethylmonochloro-silane obtained form the Rochow synthesis or by reduction of linear α,ω-dichloropoly-dimethylsiloxanes with lithium hydride.

As examples for α,ω-organofunctional siloxanes I have outlined for you the production of polydimethylsiloxanes which can be hydroxyfunctional by incorporation of an allyl alcohol with a protective group, aminofunctional by hydrosilylation of an allyl amine with a protective group or epoxyfunctional by special incorporation of allylglycidyl ether. I have further shown that epoxyfunctional siloxanes are of interest as starting products for many other functional siloxanes.

Beyond that, I have tried to present to you a few examples of the broad spectrum of possible applications of these siloxanes as soft segments in ABA or (AB)$_n$ block copolymers. The incorporations introduce the properties of the siloxane into the polymer matrix. One should note here the extremely low glass temperature of $-123\,^\circ$C, the low surface tension of $20-21$ mN/m, good thermal stability, good permeability for gases, physiological inertness and good hydrophobicity. I hope to have awakened in you an interest in these attractive products.

Bibliography

[1] Noll, W., Chemie und Technologie der Silicone, Verlag Chemie, Weinheim, (1968)
[2] Wacker, Silicone – Sand, der sich nützlich macht. 40jährige Wacker Jubiläumsschrift, (1988)
[3] DE AS 1 085 875
[4] DE PS 3 637 273
[5] Chalk, A.J. and J.F. Harrod, J. Am. Chem. Soc., **87**, 16, (1965)
[6] DE OS 3 222 839
[7] US PS 2 924 588
[8] Saam, J.C. and J.L. Speier, J. Org. Chem., **24**, 119, (1959)
[9] Yilgör, I. and J.E. McGrath, Polysiloxane Containing Copolymers, A. Survey of Recent Developments, Adv. Polymer Sci, Band 86, (1988)
[10] Kuckertz, J.H., Makrom. Chemie, **98**, 101, (1966)
[11] US PS 4 668 755; R.H. Bott et al, J. Adhesion, Band 23, 67, (1987)
[12] Yilgör, I., J.S. Riffle, G.L. Wilkes and J.E. McGrath, Polymer Bulletin, **8**, 535, (1982) and 543, (1982)
[13] Th. Goldschmidt, so far unpublished research results

Chemistry and Technology of Silicone Resins

by B. Deubzer

Introduction

Silicone resins are the third group of silicone polymers other than silicone fluids and silicone elastomers. In their case the starting materials are network forming trichloro-silanes, in some special cases and in ethylsilicates also silicontetrachlorid.

Looking at the technology of silicone resins it can be stated that in the course of development the polymeric resins have been partly substituted by oligomeric or even monomeric intermediates or that products of different molecular weight compete for the same application.

The essential point is, that in all cases more or less similar highly crosslinked networks are formed after application.

For industrial practice resins had to be soluble and/or fusible polymers. For more recent developments this requirement is outdated.

Chemistry and technology of silicone resins and their precursors

Definition

Different criteria may be used to characterize silicones:

– Functionality of educts in respect to number of Si-O-linkages formed in the polymers is described with the symbols D, T, Q and M. Crosslink density of a polymer is determined by choice of structural units.

Basic monomer	Functionality with respect to hydrolyzable groups	Structural unit in the polymer	Symbol
SiX_4	tetrafunctional	$SiO_{4/2}$	Q
$R - SiX_3$	trifunctional	$RSiO_{3/2}$	T
$R_2 - SiX_2$	difunctional	$R_2SiO_{2/2}$	D
$R_3 - SiX$	monofunctional	$R_3SiO_{1/2}$	M

Fig. 1: Structural units of silicone chemistry

- The substituents R represent the organic part of the molecule.

  Carbon content and number of constituents per silicone atom determine the techno-
  logical properties of the polymers.

- The organic substituents R may be functional groups themselves in order to provide
  reactive centers.

A molecule like vinyltrichlorosilane is as well silicon functional in respect to the hydroly-
zable Cl-groups as organofunctional in respect to the vinyl group. As a structural unit the
silane is a trifunctional or branching unit.

The term "trifunctional" has nothing to do with the number of reactive groups in the
polymer. This terminology may cause some confusion.

- Silicone combination resins are copolymers of organopolysiloxanes and organic resins
  like polyester, epoxy or alkyd.
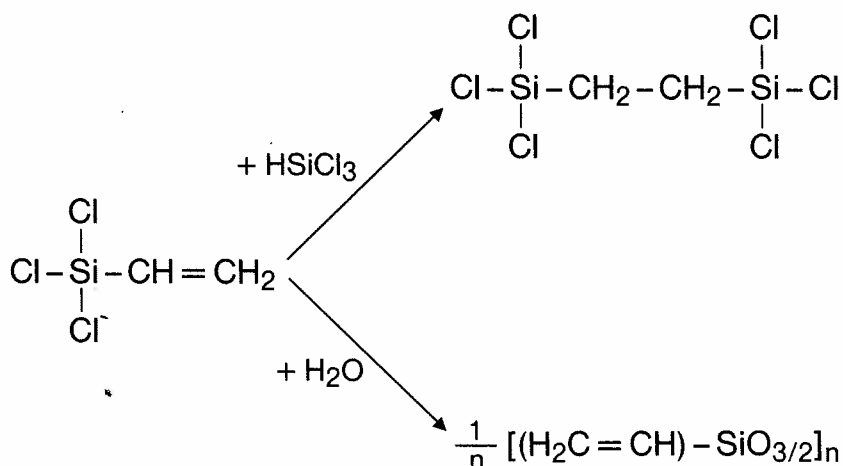
Fig. 2: Difunctional siloxanes

Classification of organopolysiloxanes based on functionality of educts

Simple permutation of the four structural units M, D, T and Q gives 15 possible com-
binations.

The units DM, DD, MM are not branched and therefore not resinous.

Resins of Q-units with M are important polymers in silicone technology. Other polymers
with Q-backbone are quite uncommon.

For technical products the combination TT, TM, TDM, TT and QQ are realized.

Obviously a few T-branches in a linear chain will not constitute the network of a resin.
With increasing T-content the viscosity of the polymer increases. The homopolymers
of the most important methyl- and phenyltrichlorosilanes are solids.

Class	Siloxane units	Class	Siloxane units
1	Q T	8	Q T M
2	Q D	9	Q D M
3	Q M	10	T D M
4	T D	11	Q T D M
5	T M	12	T T
6	D M	13	D D
7	Q T D	14	M M
		15	Q Q

according to W. Noll, Chemistry and Technology of Silicones

Fig. 3: Possible combinations of siloxane constituents

Classification of silicone resins based on organic substituents

Methyltrichlorosilane alone or in combination with other silanes is the most important monomer in silicone resin technology.

It is readily available as byproduct of the direct synthesis.

Methylsilicone resins contain the lowest amount of carbon in the resins (closest to inorganic silicates).

Phenylsilanes may be produced in different ways as f.e. by reaction of chlorobenzene with trichloro- or methylhydrogendichlorosilane (the latter being byproduct in the direct synthesis).

Introduction of phenyl groups into the polymer backbone increases the thermostability of organopolysiloxanes.

Alkyl silanes with longer hydrocarbon chains are used in the technology of silicone resines to increase the stability against decomposition by alkaline reactants. They are accessible by platinum-catalyzed addition of olefins to trichlorosilane.

Characterisation of organopolysiloxanes based on functional groups

Silicone resins with few exceptions are silicone functional, the functional groups being SiOH and/or C_1-C_4 alkoxygroups.

Curing to insoluble endproducts proceeds via polycondensation between these groups.

The reaction can be catalyzed by a wide variety of acidic or alkaline compounds. Excellent results are obtained with Sn, Pb, Al and Zn compounds as well as with organotitanates.

The proper choice of catalysts depends on application.

Standard silicone resins require quite drastic condition for curing as curing temperatures $> 150\,^\circ C$. When adding f.e. a stannous catalyst to a silicone resin solution at ambient

temperatures, gelation will occur in a short time. The gel formed in this way is a incomplete network, many silicone functional groups do not react.

For some applications it is possible, however, to use low molecular weight alkoxy-siloxanes with higher amounts of silicon functional methoxy or alkoxy groups.

In the presence of suitable catalysts they will be hydrolyzed by the humidity of the air, splitting off the corresponding alcohol. The silanols formed in this reaction are highly reactive and quickly form the desired endproducts, even at ambient temperature.

Introduction of vinyl groups into the resinous polymer clears the way to peroxidic curing. Solvent free liquid resins of this type weren't successful on the market, the main problem being stickiness of the surface due to inhibition of the cure by atmospheric oxygen.

Silicone resins with vinyl and hydrogen substituents in the same molecule can be cured by platinum catalyzed hydrosilylation.

A wide variety of publications and patents describes silicone resins with functional groups other than those discussed so far. It remains to be seen whether they will be successful on the market.

Silicon combination resins

Silicone resins of this type are blockcopolymers consisting of a preferentially phenyl rich methylphenylpolysiloxane and an organic polymer like polyester-, alkyd-, acryl- or epoxy-resin.

Copolymerisation is carried out by reacting the carbinolfunctional resins with silanol or alkoxygroups of the organopolysiloxane. Compatibility of the different polymers is a problem, which is overcome by using methylphenylpolysiloxanes with low SiO_2-content and low molecular weight intermediates on both sides.

Both components are polyfunctional. The problem of gel formation during cocondensation can be solved by lowering the effective functionality using an considerable excess of functional groups on one side.

Quantitative treatment of these cocondensation reactions has been tried in analogy to alkyd resin technology, with only moderate success.

Tailor made polymers are possible when using polysiloxanes with organofunctional groups.

Silicone resins available in technical amounts

Standard silicone resins on the market generally contain the following structural units:

Phenyl- or alkyltrichlorosilanes together with methyltrichlorosilane determine the highly branched backbone. Dimethyldi-, phenylmethyldi- and diphenyldichlorosilanes are used to flexibilize the brittle resin. Methylhydrogendichlorosilane, vinyltri- or vinylmethyl-dichlorosilane enable preparation of addition curing systems. Trimethylchlorosilane is introduced as endblocking agent.

Unmodified methylsilicone resins based on methyltrichlorosilane, sometimes flexibilized with smaller amount of dimethyldi-, or trimethylchlorosilane represent a group of their own, distinguished by incompatibility with other polymers.

There is a large number of possible combinations of structural units. Resins of different producers, which are offered on the market for the same application, are in the rarest cases chemically identical. Comparable properties can be tailor-made with quite different formulations.

MQ-resins, based on silicontetrachloride and trimethylchlorosilane, are used in special areas.

For ratios of M:Q between 0.6 and 1.0 soluble, but not fusible solids can be obtained. They have the remarkable property to be soluble in polydimethylsiloxanes of all kinds.

They are used as reinforcing fillers in transparent silicon-elastomers, as resinous component in pressure sensitive adhesives, in antifoaming compounds and other areas of silicone technology. By introduction of functional groups, generally the vinyldimethyl group, chemical bonding between the MQ-resin and a similarly functionalized PDMS-matrix can be achieved.

They are syntethized by trimethylsilylation of alcalisilicates or hydrolysis of ethylsilicates in presence of silylating agents like hexamethyldisiloxane.

From chlorosilanes to technically useful products

Understandably chlorosilanes due to their aggressive properties are used only in very rare cases as such, fe.e. for treatment of inorganic surfaces in special applications.

Generally chlorine is substituted by the monovalent alkoxy group or the divalent oxide bridge.

It was mentioned earlier, that in practical applications monomeric, oligomeric and resinous products compete for the same applications. Important is, that a highly branched endproduct is formed.

For this reason it seems appropriate to start with discussion of the conversion of chloro- into alkoxysilanes, followed by production of oligomeric and resinous products.

Alkoxysilanes from chlorosilanes

The reaction is easily formulated

$$RSiCl_3 + 3\ ROH \rightarrow RSi(OR)_3 + 3\ HCl$$
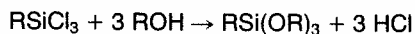
Under practical conditions side-reactions are likely to occur as f.e. reaction of residual $\equiv SiCl$ with newly formed $SiOR$ under formation of siloxanes and alkylhalogenide.

$$\equiv SiCl + \equiv SiOR \rightarrow\ \equiv Si\text{–}O\text{–}Si \equiv\ +\ RCl$$
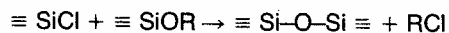
Side reactions must be pushed back by appropriate choice of experimental conditions.

The alkoxylation can be carried out in continous processes if there is demand for large quantities.

A process of this type, which uses destillation columns is described schematically in the following.

Ethanol is fed into the column shortly above the boiler. The temperature profile of the column is adjusted so, that near the top the boiling point of ethanol is surpassed. The chlorosilanes are fed into this zone. The boiling point of the chlorosilanes increases with

increasing substitution of chlorine- by alkoxygroups. Consequently the silanes drift downward, react with fresh ethanol, and the desired endproduct is collected in the boiler. After removal of unreacted ethanol, which goes back into the process, the product can be carried out. At the top of the column an excess of boiling ethanol always must be present.

Hydrogen chloride formed during alkoxylation is insoluble in the boiling mixture and is carried out at the top.

Alkoxysilanes formed in this process are free of chlorine for technical purposes (ppm-range).

If very high purity is required for special reasons, additional purification steps are necessary like destillation from alkaline halogen acceptors.

Alkoxysiloxanes from chlorosilanes

If water/ethanol mixtures are used or water is fed into the column in a suitable manner oxygen bridges can be introduced in a simple manner and oligomeric siloxanes are formed.

In principle even resinous products, which are solids when solventfree, like the homo-polycondensates of methyl- or phenyltrichlorosilane, can be prepared continously.

Continously processed are silanes like vinyltri-, methyltri- or phenyltrialkoxysilane. Quite important are ethylsilicates like ethylorthosilicat and oligomeric intermediates like TES 40, as well as oligomeric methylphenyl- and methylalkylsiloxane intermediates. The latter are used for silicon combination resins and as masonry water repellents. Loop reactors have been described for the same production.

Silicone resins from chlorosilanes

The hydrolytic preparation of silicone resins from chlorosilanes can be very easily described schematically. During hydrolysis silanolfunctional siloxanes are formed, which react further

$$nRSiCl_3 \xrightarrow{H_2O} (RSiO_{3/2})_n$$
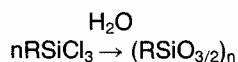
In reality the problem is more difficult. When adding water to trichlorsilanes unsoluble, unmeltable gels are rapidly formed due to the high reactivity of newly formed silanols combined with the catalytic activity of hydrochloric acid.

Gel formation must be controlled if technically useful products are to be obtained.

This can be achieved by different means as

- dilution with solvents
- type of solvent
- acid/alcohol content
- time of reaction
- temperature

Dilution with water immiscible, inert solvents like toluene withdraws the reaction products from the direct influence of hydrogen chloride and concentrated hydrochloric acid. The

dilution effect increases tendency towards intramolecular ring formation over intermolecular condensation.

The immiscibility of water- and solventphase, however, means, that hydrolysis takes place on the poorly defined boundaries of the phases and is only moderately reproducable.

Progress is achieved by use of solvents suitable for both phases like acetone. A further possibility is the addition of short chained alcohols like n-butanol. They act as solvent for both phases and diminish the reactivity by formation of alkoxysilanes.

Another process, especially used when hydrolysing the highly reactive methyltrichlorosilane, removes part of the hydrogenchloride by alkoxylation, followed by hydrolysis.

Problems may be encountered when hydrolyzing mixtures of silanes due to different speed of hydrolysis as well as differing cocondensation parameters.

Not only degree of polycondensation and nature of silicone functional groups like SiOH and SiOR are of great importance, but also the molecular weight distribution.

This is especially true for silicone resins, which are to be reacted with organic resins in a further step. Already small amounts of high molecular weight components may cause formation of gel particles or gelification of the whole batch. The molecular weight distribution can be influenced during production or changed after hydrolysis (equilibration).

In some cases it can be necessary to increase the viscosity of a resin solution in a separate step (bodying).

Most silicone resins are specialties, produced in comparatively small quantities.

Discontinous batch production prevails.

Technical products must be storage stable for at least several months. Hydrolysis has to be performed so, that no to reactive structural elements are formed. Production of special silicone resins with outstanding reactivity has to be carried out in a different way. In this case alkoxysilanes are hydrolysed.

Silicone resins from alkoxysilanes

Alkoxysilanes of the Q- and T-type can be hydrolysed in presence of solvents and traces of acids as catalysts in a very mild manner. Highly reactive resins can be prepared, which are curable already at appr. 100 °C.

Another process has been described and patented in many variations during the last years. Alkoxysilanes are hydrolysed not with water, but with silicic acid hydrosoles.

The alkoxyheteropolycondensates, which are prepared in this way, contain up to 70 weight percent of small silica particles with diameters ranging from 10 to 30 nm. Modification with organofunctional silanes or blending with organic resins is described in numerous patents too.

Resins of this type are used as scratch resistant coatings for thermoplastic resins like PMMA and PC. They also have been recommended as corrosion resistant coating for nonferrous metals.

Ready to use ethylsilicates are prepared in a similar manner and used in the foundry industry for quite a long time.

Structural elements in silicone resins

Compounds of the average formula $(RSiO_{1.5})_n$ have been described in the previous century, when chemists were looking for the silicone analoga RSiOOH of carbonic acids.

Details concerning the structural elements formed during hydrolysis were evaluated only in the second half of this century.

The literature until 1981 has been reviewed by M.J. Voronkow and V.J. Lavrent'yew in Top. Curr. Chem. 1982, 102, 199–236.

Resinous polymer are very complex. The structural elements formed during hydrolysis are influenced by

- concentration of monomer in solution
- type of solvent
- nature of organic substituent
- nature of hydrolyzable group
- type of catalyst
- temperature
- amount of water
- solubility of products

This enumeration shows that it is impossible to speak about the structure of silicone resins. It is thought that in all resins a variety of different structural elements is present.

It seems accepted, however, that at the beginning of hydrolysis cyclic structures are formed. These combine to cage-like molecules.

Under appropriate experimental conditions well defined, crystallised polycyclic molecules like octa- or decamethylsilsesquioxane $(RSiO_{1.5})_8$ and $(RSiO_{1.5})_{10}$ can be isolated.

The combination of incompletely condensated cages via corners, edges or D-units, if present, may characterise the structure of technical products.

The whole of structures present defines the technological properties of the resin. Hydrolysis of methyltrichlorosilane only under varying conditions gives either

- insoluble, non meltable solids
- in aliphatics soluble, moderately reactive resins of MW 2000–3000
- poorly soluble, highly reactive silicone resins with physical and chemical data similar to the previous ones
- well defined, crystalline silsesquioxanes
- "ladder-polymers"

Heating up of oligosilsesquioxanes or technical resins with alkaline catalysts to temperatures > 200 °C yields polymers of high MW.

Particularly well investigated are phenylsilsesquioxanes. Polymers prepared on this base are stable up to 500 °C.

A ladder structure has been discussed for these polymers (Brown et. al. 1960). Later arguments have been published against this structure. Nevertheless, up to now always

new publications and patents describe preparation and properties of silicone resin ladder polymers.

A possible field of application for these polymers, which form very hard and brittle films, seems to be microlithography.

Attempts to synthezise technically useful products by combination with PDMS have been unsuccessful so far.

Treatment of silicagel with tetraalkylammoniumhydroxid leads to formation of silicate anions in the water phase. By trimethylsilylation well defined trimethylsilylsilicates like M_8Q_8 or $M_{10}Q_{10}$ may be prepared.

Formulations of silicone resins

Silicone resins are supplied in different form, in order to be able to fulfill all requirements from the enduser.

The most important are:

- Silicone resin solutions
- Silicone resins as flakes and powders
- solventfree impregnating resins
- water borne systems

Silicone resin solutions

Solvent based systems used to be the most common form of supply.

Methyl- and methylalkyl resins may be soluble in aliphatics, depending on the resin. Standard solvents are toluene or xylene, which are required for most methylphenyl-silicone polymers.

To improve shelf life more polar cosolvents like n-butanol or cyclohexanone often are added.

In general silicone resins may be used with a wide variety of solvents without problem.

The solids content of methylresins generally is 50%, higher contents being possible, but only with reduced shelf life.

Phenylmethylresins come with solid contents between 50 and 80%.

Solid silicone resins

Silicone resins as solids are sold as flakes or powders.

Only resins with an sufficiently high softening point can be supplied in this form.

That means, that quite generally only polymers with high percentage of methyl and/or phenyl T-units are possible. D-units depress the softening point, the same is true for longer chain alkylsilanes. The softening point also depends from rather unclear structural features f.e. the conditions of hydrolysis.

Softening begins mostly around 40 to 45°C, when viewed optically in a capillary tube.

Solid silicone resins are used as binder in moulding compounds, in cements for lamp sockets, as silicone component in combination resins, as water repellent in hygroscopic products. They can be dissolved in a wide variety of solvents if needed.

Shelf life is no problem even for methylsilicone resins. It is higher than that for high solids solutions. This is probably due to reduced mobility of reactive groups in the solid resin.

Solventfree impregnating resins

Oligomeric methoxy- and ethoxy-silicone functional organosilicones are fluids at R to Si ratio of 1.0 and degree of polymerisation of 3 to 10.

They will hydrolyse in the presence of atmospheric humidity and catalysts. End products are resinous polymers. Monomeric alkoxysilanes or mixtures thereof react in a similar manner. Due to high vapour pressure product losses may arise during application.

Oligomeric alkoxysiloxanes finally are preferred building blocks for the reaction with carbinolfunctional organic resins.

Cocondensation can be better controlled than the analogous synthesis with silanols under formation of water.

In presence of D- and endblocking M-units in sufficient numbers the polymer backbone becomes less rigid. It is possible to prepare highly branched but nevertheless liquid systems without hydrolysable end groups. Resins, which contain reactive centers in form of vinyl- and Si-hydrogen groups, can be cured blisterfree even in thick layers by the addition curing mechanism.

Water-borne systems

For years pressure has mounted to substitute solvent-containing systems for reason of safety-related and ecological considerations. An alternative are water borne systems.

What is available in silicone chemistry?

Alkalisiliconates

The most important products are the alkalisiliconates.

When methyltrichlorosilane is hydrolysed, the hydrolysate washed until free of acid and dissolved with sodium- or better potassiumhydroxid, stable waterbased and water dilutable alkalisiliconate solutions are obtained (ratio 1 mol alkalihydroxid to 1 g atom Si). The designation was formed in analogy to the well known alkalisilicates.

After application carbondioxide from the atmosphere will react under formation of the corresponding alkalicarbonate on one side, highly reactive and quickly further polymerizing silanols on the other side.

The solubility decreases rapidly with increasing carbon content of the organic substituent. For this reason other than methylsiliconates only propylsiliconates have gained technical importance. The most important field of application are masonry water repellents.

A disadvantage of alkylsiliconates is the aggressive character of the strongly alkaline solution as well as the formation of considerable amount of inorganic salts during cure.

Silicone resin emulsions

Silicone resins may be emulsified like other polymers in the presence of suitable emulsifiers under high shear rates. There are some technological limitations. Dispersions of solid resins in water have been described in the literature. Generally however solid or very viscous resins have to be emulsified in the presence of some solvent. With solid resins at least around 20 weight % of solvent are necessary. Completely solventfree systems are difficult to prepare.

The amount of D-units may be increased until the viscosity of the polymer is low enough to be emulsified with only small amounts of solvents or even solvent-free. Polymers of this type tend to be sticky after evaporation of the water phase. This may be prohibitive in many applications.

An alternative are emulsions with alkoxysiloxanes as dispersed phase.

It is surprising but possible, to emulsify longer-chain alkoxysiloxanes or even the corresponding silanes with good shelf life and no gel formation.

Silicone resin microemulsions

Classical silicone emulsions require a certain amount of emulsifier, the shelf life is limited. Properties can be improved by drastic reduction of the particle diameter of the dispersed phase. These systems are called microemulsions.

With particle diameter lower than the wave length of visible light these emulsion can be water clear. Generally high emulsifier concentrations are required, up to 20−30 weight percent, based on content of the dispersed phase.

There are alternatives in silicone resin technology.

Alkoxysilanes of the T-type can be hydrolyzed with a large excess of water in the presence of suitable additives, which can act as catalysts and emulsifiers.

Suitable microemulsions or hydrosoles with crosslinked resinous particles are obtained (Lekada 1962). The process is rather variable in respect to particle structure.

Another possibility is to incorporate aminofunctional silans into the backbone of D, T and Q polymers. By acidifying with f.e. acetic acid highly polar ammonium salts are formed. These "silicone surfactants" can be used to emulsify other alkoxysilanes or alkoxysiloxanes. In the presence of cotenside microemulsions are formed spontaneously upon dilution with water. After evaporation of water and acetic acid, water insoluble, hydrophobic silicone resin are formed. Fields of application are masonry water repellants and primer for latex paints.

The solid content of microemulsions is limited to about 20 weight %. At higher concentrations there is a rapid increase of viscosity, the phenomenon depending from particle size.

Master-batch process

Some alkoxysilanes dissolve more or less rapidly in water, when acidic catalysts are present.

Solubility and shelf life of the solution depend from the organic substituent. Generally only a few hours of shelf life can be expected.

Applications of silicone resins and their precursors

Applications of silicone resins can be divided into three temperature ranges. For each range silicone resins show typical behaviour.

– Applications at temperatures exceeding 400°C characterized by pyrogenic formation of silica and reactions thereof.

– Applications at temperatures up to 300°C whereas the polysiloxane molecule is more or less stable.

– Applications at ambient temperatures.
Excellent wetting properties and hydrophobizity of silicones are main area of interest.

Applications exceeding 400°C

At temperatures above 400°C the organic substituents of organopolysiloxanes are rapidly oxidized in presence of air. Moreover low molecular, volatile compounds, either present in the resin or formed by thermal depolymerization, may evaporate. The latter can be reduced by appropriate choice of curing catalysts. This is important for practical work.

The silicone-oxygen backbone is in contrast to the organic substituents not influenced by this oxydation.

When heating up silicone resins, white silica powder is formed, which cannot act as binder in this form.

Silicone resins, however, are generally processed, like many other resins together with pigments, fillers and reinforcing materials of various kind.

The pyrogenic silica, which is formed during thermal decomposition of the silicone resin, is thought to be able to sinter at temperature above 400°C with other heat stable components in the systems. New composites are formed, which can fulfill the requirements at even higher temperatures.

Two examples may illustrate applications of this type:

In the industry mica is highly estimated as an excellent, long term temperature resistant electrical insulating material.

Mica splittings can be transformed into very fine leaflets by different industrial proceedings. Water based slurries of these leaflets are used to produce mica paper. This paper is impregnated with resin solution and the solvent evaporated.

The prepreg so formed has a certain shelf life. In an alternative process the resin may be incorporated as a powder during the paper production.

In the last step several layers of prepregs are cured under heat and pressure to form mica sheets of the desired dimension. Supporting bases for the wire of resistance heatings are punched out of these mica sheets.

Methylsilicone resins have gained worldwide acceptance for this application.

They are easily processed, there is a minimum of weight-loss when heating up for the first time and a maximum of pyrogenic silicone is formed.

Another example are aluminum pigmented paints. For the same mechanism as already described they can be used as long time corrosion resistant paints for temperatures up to 600 °C. For similar applications micaceous iron oxide pigments are used, too.

In both examples lamellar pigments are used, which form dense, closely packed layers. Compounds with spherical particles are less suited to form such films. This means, that decorative paints for this temperature are more difficult to obtain.

One may conclude from the foregoing discussion, that methyl silicone resins are the materials of choice for heat resistant paints in general.

This is not always the case, as will be explained later.

Application of silicone resins at temperatures up to 300 °C

Historically the search for heat resistant binders for glass laminates in electrical applications was the starting point for silicon technology.

Methylphenylresins are mostly used for this application, as well as in cements for lamp sockets, impregnation of glass sleevings, moulding compounds for encapsulation of electronic devices and other highly specialized problems.

An important area are heat resistant decorative coatings for industrial as well as consumer products like pots and pans, stoves etc.

In regard to paint technology methylphenylresins offer some advantages compared to methyl resins. Pigment carrying properties, elasticity, adhesion, gloss are better.

They can withstand about 50 °C higher peak temperatures.

Even better results in many properties are possible with silicon combination resins. In this type of polymers up to 50 weight percent of organopolysiloxane are substituted by an organic polymer, mostly polyester resins based on terephthalic acid, trimethylolpropane and other polyols. With increasing organic fraction there is a tendency of yellowing at peak temperatures.

In the preceeding sections it has been discussed, that at temperatures exceeding 300 °C thermal decomposition of the resins becomes an important factor whereas sinter processes start only at temperatures exceeding 400 °C. The range in between poses problems.

Even high temperature installations often reach their peak temperatures only after prolonged periodes at lower temperatures. The paint may deteriorate before sintering starts. Phenylrich silicone resins generally survive better than the harder and more brittle methyl resins. Therefore they offer increased safety in performance.

Applications of silicone resins at ambient temperatures

Silicone resins are an important part of the product group "heat resistant polymers".

In contrast to many other products of this class silicone resins are often used for applications at ambient temperature.

Simplified there are two reasons.

The silanol groups either present in organopolysiloxane molecules or formed in situ by hydrolysis of alkoxy groups are able to form covalent bonds with SiOH or COH-groups at the surface of many substrates. Moreover the Si-O-Si backbone has a high affinity to many substrates. Silicone resins are adsorbed and adhere very well with or also often without subsequent chemical bonding. At the same time the organic substituentes are oriented away from the surface. Excellent and long lasting hydrophobizity is the result even at low concentration and on many surfaces like pigments, fillers, etc.

The second point is, that silicone resins are very stable against decomposition by environmental factors. The result is excellent life time and use of silicone resins as masonry water repellants and as binder or part of the binder system in paints.

Application as masonry water repellent

Silicone resins are used for protection of pharmaceutical products, which are sensitive to moisture. They are also used to impregnate briquets pressed of coal in order to enable storage in the open air.

By far the most important market are masonry water repellents.

At our lattitudes water is the biggest enemy of all buildings, partly due to it's physical and chemical properties like the ability to dissolve mineralic components or the rupture effect when freezing. Noxious substances like acidic gases or salts are carried into building materials.

Water is essential for the growth of microorganisms which themselves can produce very aggressive metabolism products, even nitric or sulfuric acid.

Effectful masonry water repellents must adhere well to the substrate. They should not be washed out. The product must penetrate deeply into the pores. They must resist decomposition by atmospheric factors in the same way as the attack of microorganisms.

The latter must be achieved without toxic additives.

Economics require that protection is possible with small amounts of the material.

Silicone resins fullfill all requirements in an outstanding manner. Sensitivity of methyl silicones against attack by alkalinity can be overcome by modification with longer chain alkyl groups.

Silicone resins are well established for inplant production of building materials like gypsum, aerated concrete or ceramic products. Buildings are protected by masonry water repellents. Treatment of concrete bridges, parking structures etc. prevents migration of chloride ions into the concrete and thereby corrosion of the steel.

Silicone resins as binder in paints

Copolymers of silicone and organic resins with silicone weightparts up to about 30% exhibit significant improvement in gloss retention and chalking.

Typical applications are coil-coated metal sheets or silicone alkyds for military and civilian vehicles and ship paints.

In the last time a basically rather old application has found new and great interest.

Silicone resins in dispersion paints for the building industry.

Silicone resin paints have some unique advantages compared to the well known latex or silicate paints:

They are impermeable to water, but open to water vapour.

They can be applied with conventional equipment and have the long life time of silicones. Coloured systems are no problem, the appearance is mineral-like as required by the present trend.

Application of silicic acid esters

Paint industry

Silicic acid esters, mostly ethylsilicates, are established as binders for zinc-rich paints. They cure even under unfavourable conditions quickly to solvent resistant, well adhering and easily overpaintable coatings.

Due to cathodic protection and selfsealing effects under-rusting even in problem areas like edges and defects is prevented.

Ethylsilicates themselves cure to slowly in air. For practical purposes they are hydrolysed further after addition of solvents and mostly acidic catalysts.

The ready-to-use binder have a shelf-life of about 24 hours in presence of zinc pigment. They are offered as two component systems.

A newer development are one pack systems. They cure after contact with the atmospheric humidity.

Fields of application are ship building industry, off-shore drilling rigs, industrial constructions, container, pipe lines.

Foundry industry

The foundry industry is an important field of application for ethylsilicates.

They are used as binders for composites with zirconium silicates, quartz, crushed quartz glass, alumosilicates and aluminas. Precision casting requires refractory moulds and cores of this type.

In the lost-wax process, wax models are coated with refractory layers of the composites mentioned above. After melting out the wax and firing the mould is ready for precision casting. Even complicated parts can be made with high accuracy and quality.

Stone strengtheners

Buildings and monuments of mankind decay with passing time.

Consciousness of the obligation to pass on the cultural heritage to future generations increases. As a consequence there is a demand to repair and protect such monuments.

Unsufficiently tested, hastily applied concepts have caused negative results in the past. A chemical treatment should strengthen weathered areas of the building material, it should not change the overall chemical composition more than absolutely necessary and it should not impede future treatments.

Silicic acid esters, by the way proposed for this purpose already 100 years ago, fulfill all requirements in an autstanding manner. In combination with solvents and suitable catalysts systems with low viscosity can be formulated, which penetrate into the weathered stones as required. Reaction with atmospheric humidity gives neutral silica gels. The latter are completely inorganic, mineral-like binders for strengthening damaged parts.

Addition of water repellent siloxanes provides protection against further damage.

Not only properly formulated products are necessary. Extensive know-how is required to achieve the desired results.

Newer developments

In the classical technology of silicone resins it was necessary to produce soluble and fusible products, in analogy to other polymers.

Gel-formation during production or storage excluded further use.

Properties and potential applications of gels became object of intensive studies only in recent years.

The sol-gel-process

Silicic acid esters, T-silanes or mixtures thereof form initially after addition of water and in presence of appropriate catalysts clear solutions. These solutions will form a gel more or less rapidly.

It was found, that the structure of the gels depends from a variety of parameters like:

— catalyst (pH-value)
— ratio water to alkoxy silane
— solvent
— starting material
— temperature
— chemical additives

Hydrolysis under acidic conditions f.e. leads to quick and complete reaction, provided enough water is present. With increasing degree of hydrolysis the reaction rate decreases. Linear structures are formed preferentially.

Under alkaline conditions hydrolysis will be incomplete, polycondensates will redisolve, rearrangements and transesterifications take place. Reaction rate increases with increasing degree of hydrolysis.

Highly branched structures appear in addition to unreacted silanes.

The decisive problem is transformation of tailor-made gel structures into technically useful products.

Simplified there are three possibilities:

— drying of gels with full conservation of the pore structure

- drying to dense, pore-free bodies
- drying and formation of a defined porosity

All possibilities have been realized.

Drying under supercritical conditions preserves the pore structure and gives transparent inorganic foams with a degree of porosity up to 99% and unusual properties.

Drying of linear, interwined structures gives dense, drying of networks of random agglomerates gives highly porous films and bodies.

Networks of defined, uniform particles may be dried to advanced materials with controlled porosity.

Via alkoxides of elements other than silicone a variety of heteroatoms may be incorporated in homogenous reaction. Glasses and ceramics are accessible without the requirement to melt the components.

Inorganic materials can be processed by chemical means using liquid, soluble or dispersed precursors.

Researchers are looking for glass and ceramic fibres, -powders, -films, -coatings, -composites, porous ceramics, aerogels, composites of inorganic and organic provenience including organofunctional silanes.

Possible applications are synthetic quartz, glass cables, optical elements, filter, catalyst support, nuclear fuels, supraconductors, scratch resistant, antireflective and insulating coatings.

It has been estimated, that the present market volume of 25−50 Million US $ will increase to 300−500 Mio until 1993.

Organopolysiloxane particles

Surface modification of inorganic materials with organofunctional silanes is state of the art.

This process has fundamental draw backs. The density of hydroxyl groups at the surface is in most cases limited. Accordingly low is the amount of functional groups bound after silanisation. Furthermore, these groups are quite sensitive to hydrolytic scission.

An alternative is the production of organofunctionalyzed polycondensates via sol-gel process, drying, grinding and classification of the particles.

Recently spherical particles with narrow particle size distribution and defined porosity have been described.

The particle diameter vary between a few nanometers up to mikrometer range, specific surfaces accordingly from a few to several hundred m^2/g.

Resins of this type are discussed as catalyst supports and ion exchangers, also as tailor-made siloxane fillers and additives for paints, elastomers, duro- and thermoplastic polymers.

The future will show whether these products will be successfull on the markets.

Bibliography

[1] Rochow, E.G.: Silicon and Silicones. Springer Verlag, Berlin Heidelberg (1987)
[2] Voronkov, M.G. and V.I. Lavrent'yev: Top. Curr. Chem. (1982) 102, 199−236
[3] Weber, H.: Steinkonservierung. Expert-Verlag, Ehningen
[4] Weber, H.: Fassadenschutz und Bausanierung. Expert-Verlag, Ehningen
[5] Dislich, H.: Journal of Non-Crystalline Solids, 73, (1985) 599−612
[6] Sowman, H.G.: Ceramic Bulletin, Vol. 67, No. 12 (1988) 1911−1916
[7] Sakka, S.: Ceramic Bulletin, Vol. 64, No. 11 (1985) 1463−1466
[8] Johnson, D.W.: Ceramic Bulletin, Vol. 64, No. 12 (1985) 1597−1602

Chemistry and Technology of Silicone Surfactants

by B. Grüning

Silicone surfactants form a group of oligomer surfactants whose development started with the use of silicone polyether copolymers as stabilizers for polyurethane foam. Since then, silicone surfactants have proven themselves as the special surfactants of choice for many other applications. Examples are their use as auxiliaries in the textile industry, in cosmetic products and as paint additives. The opening up of new fields of application is closely tied in with the development of new silicone surfactants. Thus, in addition to silicone polyethers, there are silicone surfactants that contain lipophilic alkyl groups or hydrophilic ionic groups.

Silicone Oils as Surfactants

The basis for silicone surfactants is polydimethylsiloxane. Its special physical-chemical properties characterize the silicone surfactants. Thus silicone surfactants exhibit an outstanding surface activity. This is caused by the incompatibilty of polydimethylsiloxane with water and many polar and nonpolar organic media and by the low surface tension of polydimethylsiloxanes of about 20 mN/m. The surface activity is not restricted to aqueous systems; silicone surfactants are surface-active also in organic media. In this respect, they clearly surpass organic surfactants and only the fluorocarbon surfactants can achieve a higher surface activity.

In contrast to low-molecular weight surfactants silicone surfactants need not consist of clearly separated hydrophilic and hydrophobic – or better and more generally – of lyophilic and lyophobic constituents. The necessary condition to achieve surface activity is selective incompatibility which can also be obtained – at least in a suitable medium – with pure polydimethylsiloxanes solely by proper choice of the molecular weight. One condition is that these silicone oils exhibit quite narrow molecular weight distributions.

An example clarifies the use of pure silicone oils as surfactants. This is the addition of narrow silicone oil fractions to so-called high-resilience polyurethane foams. The silicone oils regulate the size of the cells [1]. The effectiveness of polydimethylsiloxane depends on the medium and also on the molecular weight of the siloxane: if the molecular weight is too low then the siloxane is much too easily soluble and no surface activity is observed; if the molecular weight is increased to near the solubility limit, the silicone becomes surface-active and can lead to foam stabilization; if the molecular weight is further increased, the range of insolubility is reached and a foam-reducing effect is observed [2]. This example makes clear how much the surface-active properties of silicone surfactants are affected by the molecular weight of the silicone chain.

The tolerance between desirable and undesirable effects for such silicone oil fractions is understandably small – it can be extraordinarily widened by introducing lyophilic groups into the polydimethylsiloxane molecule.

In addition to its particularly pronounced surface activity, the polydimethylsiloxane radical is also responsible for other esteemed properties of silicone surfactants, such as friction

reduction i.e. lubrication, release ability and conditioning and softening of textiles and hair [3]. These qualities can be more or less marked depending on the structure of the surfactants. The high mobility of polydimethylsiloxane chains and the small tendency to form crystalline interactions is certainly basically related to these technically often used properties of silicone surfactants. For some applications, the temperature stability of the polydimethylsiloxane chain is also of importance.

Synthesis

The physical and physical chemical properties are not the only reason for the success of silicone surfactants. Of at least equal importance are the special chemical conditions which permit the production of an extraordinary variety of silicone surfactants with high reproducibility and reliability. This fact is particularly important because silicone surfactants are mostly oligomer or polymer products.

The fundamental building blocks for the production of silicone surfactants are shown in Fig. 1. They are functional polydimethylsiloxanes with reactive centers formed by Si-Cl, Si-OR or Si-H groups. The equilibration reaction [3], which is an essential characteristic of silicone chemistry, permits the production of these building blocks with high precision and reproducibility. Type 1 has a linear structure. The functional groups X are bonded terminally

$X = $ functional group
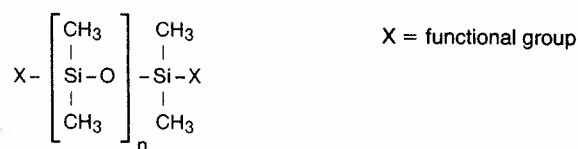
Type 1: linear, terminally difunctional
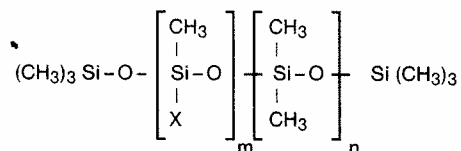
Type 2: comb-like, linear, laterally functional
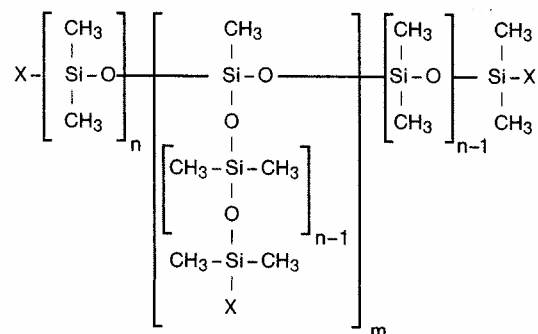
Type 3: branched, terminally functional

Fig. 1: Fundamental building blocks of silicone surfactants

in α,ω-positions. It is possible, starting from this type, to obtain polymer surfactants in which every molecule is definitely difunctional; thus surfactants resulting from this raw material strictly show the general structure ABA, where A is the compatible residue and B the polydimethylsiloxane fraction. However, it is also possible to build block copolymers of higher molecular weight with alternating lyophilic and lyophobic regions if the siloxane building blocks react with likewise linear α,ω-functional reaction partners. Such a surfactant type would then be built up of repeating AB units. In Type 2, the reactive groups are bonded laterally to the linear polymer backbone like a comb. The lateral groups are distributed in accordance with the equilibration reaction. In Type 3, the siloxane spine is branched, while in Types 1 and 2 it is linear, and the reactive centers are situated in terminal positions as in Type 1.

Si-Cl and Si-OR-groups of the building blocks can react with hydroxyfunctional partners, such as polyethers or fatty alcohols [4] as shown in Fig. 2. These esterifications and transesterifications proceed always with very good yields, and side reactions can practically be avoided with the right choice of the reaction conditions. Next to the equilibration reaction, this is a further important requirement for the precise synthesis of tailor-made silicone surfactants.

Particularly in acidic or alkaline solutions the Si-O-C bond obtained in this manner is not permanently stable with respect to hydrolysis so that the use of silicone surfactants of this type in aqueous media is limited to the neutral pH-range. Generally in water-free organic systems, silicone surfactants obtained by esterification or transesterification reactions can be used without any difficulties.

$$\begin{array}{c} CH_3 \\ | \\ ----O-Si-X \\ | \\ CH_3 \end{array}$$

Esterification
$X = Cl$ or $SO_4/2$
$+ ROH/NH_3$
$- NH_4X$

Transesterification
$X = CH_3O, C_2H_5O$
$+ ROH$
$- XH$

$$\begin{array}{c} CH_3 \\ | \\ ----O-Si-O\,R \\ | \\ CH_3 \end{array}$$

e.g.,
R = polyether radical of $HO-(C_2H_4O)_P(C_3H_6O)_q\,CH_3$
long-chained alkyl radical of $HO-C_{18}H_{37}$
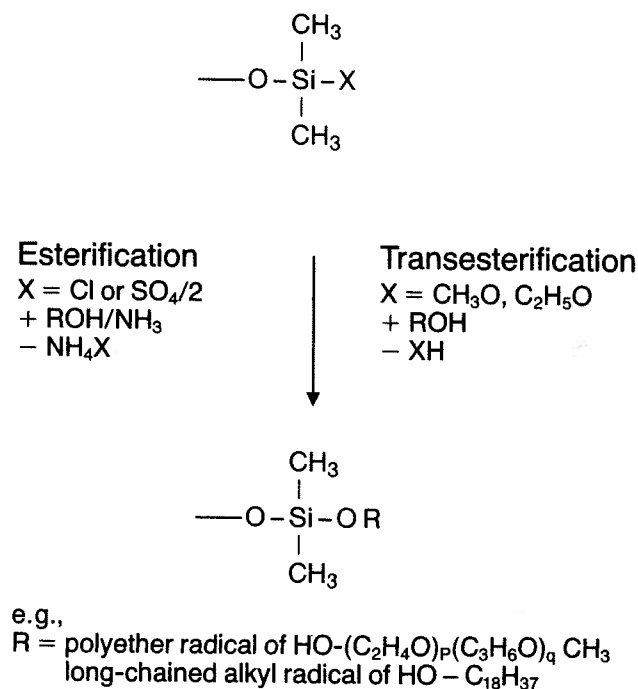
Fig. 2: Esterification/transesterification

$$\underset{\underset{H}{|}}{\overset{\overset{CH_3}{|}}{\sim\!\!\sim\!\!Si\!-\!O\!\sim\!\!\sim}} + CH_2 = CH\!-\!R$$

Pt-catalyst

$$\underset{\underset{\underset{\underset{R}{|}}{CH_2}}{\underset{\underset{|}{CH_2}}{|}}}{\overset{\overset{CH_3}{|}}{\sim\!\!\sim\!\!Si\!-\!O\!\sim\!\!\sim}}$$

e.g.
R = polyether radical of $CH_2 = CH\!-\!CH_2\!-\!O\!-\!(C_2H_4O)_P\,(C_3H_6O)_q\,H$
long-chained alkyl radical of $CH_2 = CH\!-\!(CH_2)_{15}CH_3$
epoxy-functional radical of $CH_2 = CH\!-\!CH_2\!-\!O\!-\!CH_2\!-\!\underset{\diagdown O \diagup}{CH}\!-\!CH_2$
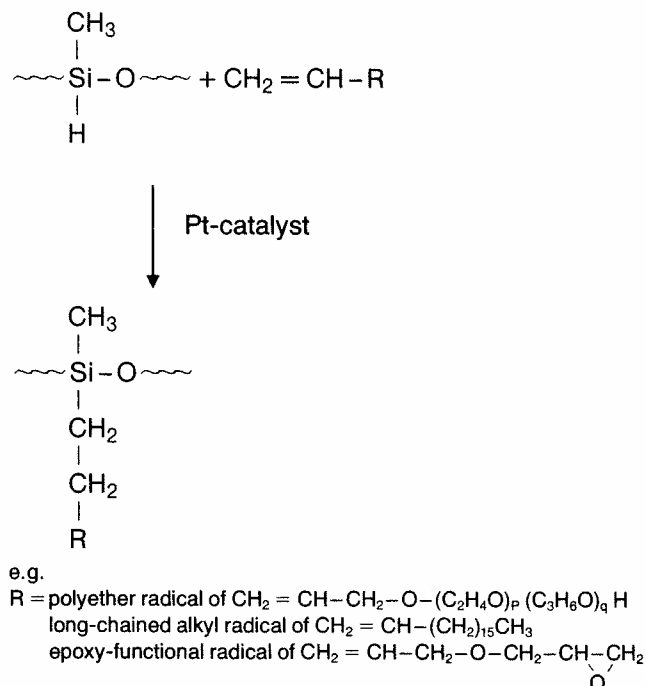
Fig. 3: Hydrosilylation reaction

A hydrolytically stable Si-C bond between the polydimethylsiloxane residue and a modifying group is obtainable by the hydrosilylation reaction (Fig. 3). Hydrosilylation can also be performed with precision and very good yields. Here, the Si-H-functional siloxanes react with terminally unsaturated organic reaction partners in the presence of transition-metal catalysts. The unsaturated compounds are mostly added in some excess to assure complete reaction of the Si-H-groups.

Using allylpolyethers organophilic or nonionic hydrophilic groups can be introduced into the molecule. By reaction with α-olefines polydimethylsiloxane is modified with organophilic, primarily mineral-oil compatible, groups; finally, by reaction with allylglycidyl ether, one can introduce reactive epoxy groups into the molecule which are easily susceptible to further reactions [4].

So ionic silicone surfactants can be obtained by ring-opening reactions from epoxy-functional siloxanes with suitable nucleophilic reagents (Fig. 4).

Reaction with tertiary amines in the presence of acids leads to formation of siloxanes with quaternary ammonium groups [5]. If a secondary amine is used, the siloxane with tertiary amino groups formed in the primary step can subsequently be transformed with sodium chloroacetate to a betaine [6]. Anionic surfactants can be obtained by the reaction of epoxysiloxanes with sodium bisulfite [7]. Also the Bunte salts formed with sodium thiosulfate are further examples of anionic surfactants [8]. All these reactions for producing ionogenic silicone surfactants from epoxyfunctional siloxanes suffer from the problem that two immiscible substances must be made to react with each other. This is
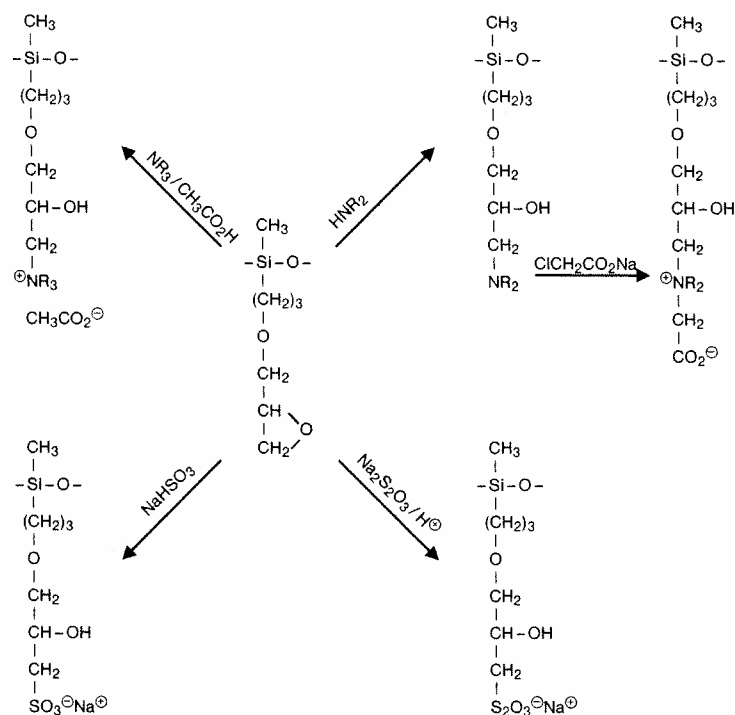
Fig. 4: Synthesis of ionogenic silicone surfactants of epoxyfunctional siloxanes

particularly marked in the production of sulfonates and Bunte salts. With increasing molecular weight of the epoxyfunctional siloxanes, these problems of incompatibility increase so that, generally, low-molecular silicone surfactants are easier to produce than higher-molecular ones.

With the aid of transesterification or esterification as well as hydrosilylation it is possible to produce a variety of differently modified silicones. As further examples one should mention amino, ester or fluorocarbon radicals that can be bonded to the siloxane molecule by an alkylene bridge.

The most important group of silicone surfactants is constituted by the silicone polyether copolymers. The Si-O-C and Si-C bonded products are of approximately equal economic importance. A summary of the physical properties of some water-soluble silicone polyether copolymers is shown in Fig. 5.

Application and Physical Chemical Aspects

Silicone Polyether Copolymers

The success of the silicone surfactants started in the late 1950's with the production of silicone polyether copolymers by Union Carbide in the USA and their application as foam stabilizers. The use of these nonionic silicone surfactants in polyurethane foams has

$(CH_3)_3\,Si-O \left[\begin{array}{c} CH_3 \\ | \\ Si-O \\ | \\ CH_3 \end{array} \right]_n \left[\begin{array}{c} CH_3 \\ | \\ Si-O \\ | \end{array} \right]_m Si(CH_3)_3$

$(CH_2)_3-O-(C_2H_4O)_p-(C_3H_6O)_q-H$
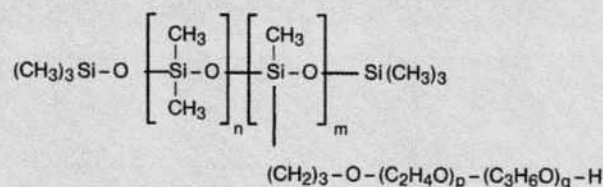
n/m value	0/1	13/5	20/5	20/5	20/5
weight-% EO/PO in polyether	80/20	100/0	75/25	35/65	20/80
cloud point, 1% in H_2O, °C	45	90	65	30	10
HLB value		19	18	14	10
solubility in water at 25 °C	+	+	+	+	−
in ethanol	+	+	+	+	+
in mineral oil	−	−	−	−	+
surface tension 1% in H_2O, mN · m^{-1}	23	28	28	27	
surface tension 1% in polypropyleneoxide*, mN · m^{-1}	27	25	25	27	27
foam height, Ross Miles in mm, at 0.1%	200	110	60	60	5

* surface tension polypropyleneoxide (molecular weight about 2000) 31 mN · m^{-1}

Fig. 5: Composition and properties of selected polyether siloxanes

decisively contributed to the importance of silicone polyether copolymers. Of course, polyurethane foam stabilizers have been developed further, but the basic principle of their effectiveness has not changed. It results from the very specific activity of silicone surfactants at surfaces and interfaces of the organic medium which consists of the reacting system of polyetherpolyol, isocyanate and a minor amount of water. Foam stabilizers control the foam structure. Particularly in flexible polyurethane foams, they can counteract the destabilizing action of the small particle sized polyurea which is precipitated as the reaction progresses. This is achieved by physical interactions. So stable foams are created which still have open cells [9].

Applications of surface active polyether polysiloxane copolymers are not restricted to use for polyurethane foams. In this sense, the table gives a survey of silicone polyethers which also find applications in other fields, e.g., in the cosmetic, textile and paint industries. Their physical properties are determined both by the kind of silicone chain, i.e., the indices m and n, and the oxyethylene/oxypropylene ratio.

The silicone polyethers listed in the table are soluble and surface active in water and polar organic liquids. Addition of 1−2% lowers the surface tension of water to 22−28 mN/m and that of a polypropyleneoxide polyether from 31 mN/m to about 26 mN/m. The trisiloxane surfactant with n = 0 and m = 1 is an excellent wetting agent particularly in aqueous media.

Silicone polyethers, in addition to pure polydimethylsiloxanes, also form the basis for many defoaming compositions. On this foundation, defoaming compositions have been developed not only for aqueous but also for organic systems, e.g., diesel oil.

$$H_{19}C_9 - \langle O \rangle -O-CH_2-\overset{\overset{\displaystyle CH_3}{|}}{CH}-O- \left[\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{Si}}-O \right]_{15} -\overset{\overset{\displaystyle CH_3}{|}}{CH}-CH_2-O- \langle O \rangle -C_9H_{19}$$
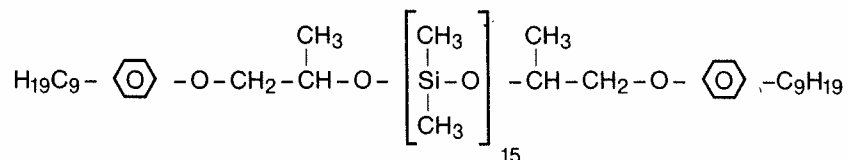
Fig. 6: Nonylphenoxy siloxane

Alkyl Modified Silicones and Silicone Polyethers

Silicone surfactants which are soluble also in nonpolar organic media, such as mineral oil, can be obtained by modification of polydimethylsiloxanes with alkyl groups or similar residues. A linear siloxane modified with nonylphenoxy groups is shown in Fig. 6. With 1−2% of this silicone surfactant one can lower the surface tension of mineral oil from 27 mN/m to 24 mN/m. This does not seem like much but indicates the presence of silicone surfactant at the surface. Such organophilic silicone surfactants can be used as additives for adhesives to achieve a marked improvement of wetting properties. In this manner, one can decisively improve adhesion to difficult substrates.

Thanks to the building-block principle according to which silicone surfactants are put together, it is also possible to combine hydrophilic polyether radicals and oleophilic alkyl radicals into one silicone copolymer. An example of this is shown in Fig. 7.

$$PE = (-C_2H_4O)_p(-C_3H_6O)_q - H$$

polyether groups

siloxane
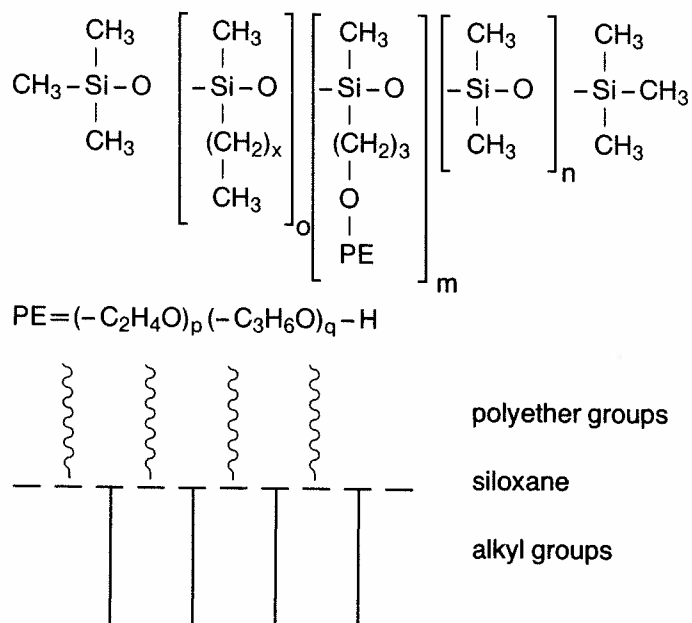
alkyl groups

Fig. 7: Silicone polyether with long-chained alkyl groups as W/O emulsifier

Silicone surfactants have a very flexible — namely liquid — hydrophobic residue which, in contrast to long-chained alkyl radicals, is not lipophilic and is much less able to form stable barrier layers. These also may be the reasons why silicone surfactants are not often used as emulsifiers. With an additional introduction of long-chained alkyl groups into a silicone polyether, one obtains a very effective W/O emulsifier [10]. Thus these silicone polyethers are characterized by the combination of three structural elements, namely, a methylsiloxane fraction, the long-chained alkyl groups bonded to Si atoms and a hydrophilic polyether fraction. The schematic presentation in the lower part of Fig. 7 shows how one can imagine the arrangement of the emulsifier at the phase boundary. The relatively high-molecular character of the emulsifier assures that it is much more difficult to desorb from the phase boundary than would be the case for a relatively lower-molecular surfactant. Thus, the reasons for the special effectiveness of the emulsifier are its surface activity, its content of alkyl groups with their compatibility with organic materials, and their ability to form stable boundary films and its polymer character. So far, the emulsifier has been used primarily in the production of cosmetic creams and lotions.

Ionic Silicone Surfactants

Silicone polyethers and alkyl modified silicones and silicone polyethers represent important types of silicone surfactants. Whereas ionic silicone surfactants are still growing in importance. In this connection, one must mention particularly the silicone quats. Effects which follow from the physical properties of the silicone residue are in the forefront of the application of these products. Most prominent effects are friction reduction
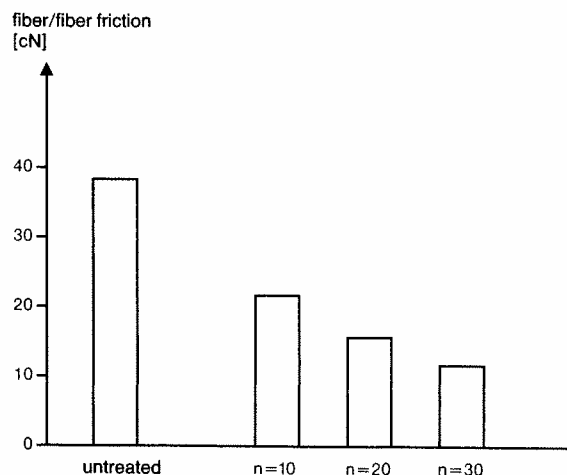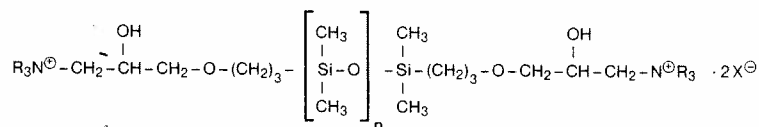
Fig. 8: Fiber/fiber friction of wool yarn treated with 0.5% silicone quat

and conditioning and softening of textiles and human hair. For cosmetic applications, improvement of gloss also plays an important role. The friction values shown in the graph of Fig. 8 were obtained during tests of fiber/fiber friction of wool yarn. The wool yarn was treated with linear, terminally quaternary silicone surfactants of various silicone chain lengths. The friction-reducing effect of the siloxane chain is clearly recognizable. The quaternary ammonium group, for its part, gives high substantivity to the silicone quats on the fiber material and is responsible for the antistatic effectiveness of the finish.

Silicone quats are also remarkable because they cause little irritation of skin and mucous membranes. Compatibility can be further improved by introducing betaine groups into the molecule instead of quaternary ammonium groups. This, however, leads to reduced substantivity.

Improvement of the feel and condition of hair is also in the forefront of the application of a new group of products: the silicone Bunte salts, also called silicone thiosulfates. The Bunte salt group undergoes further reactions under the influence of mercaptofunctional additives. These reactions finally lead to the formation of disulfide bridges. Examples of suitable mercaptofunctional compounds are thioglycolic acid or cysteine. It is possible that, in this respect, also the SH-groups of hair are active. If the silicone thiosulfate is more than difunctional, the formation of an insoluble polymer network will result. During
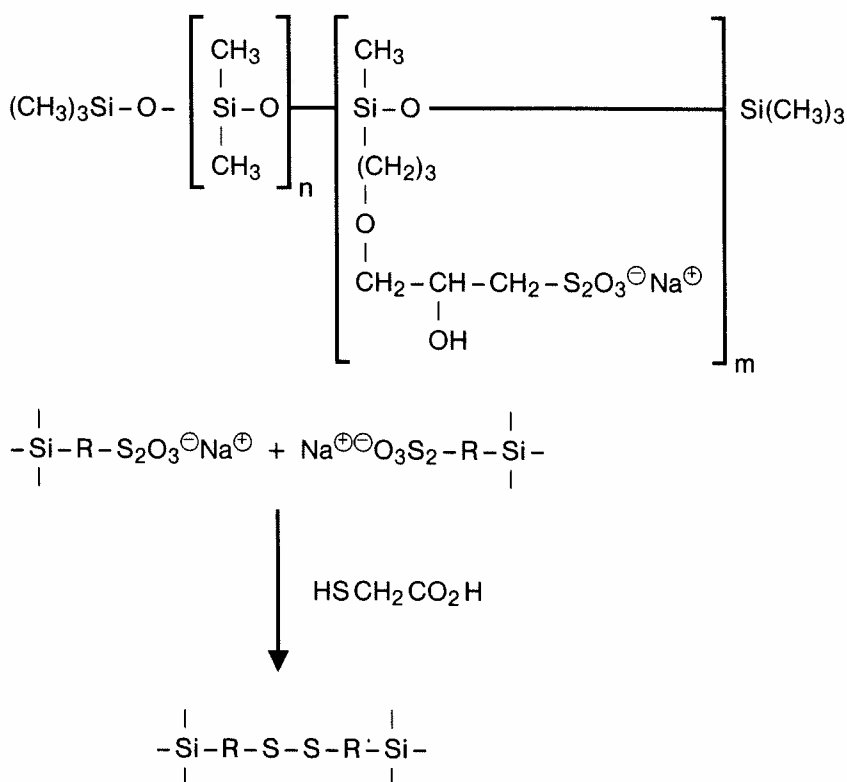
Fig. 9: Silicone thiosulfates and their cross-linkage

this process silicone Bunte salts lose their hydrophilic group and with it their surfactant properties. The resultant polymer networks are hydrophobic. There is reason to hope that silicone thiosulfates will offer interesting development possibilities for the treatment of hair and possibly also of wool.

Trisiloxane Surfactants

The outstanding surface active properties of silicone surfactants are demonstrated in Fig. 10. Water soluble trisiloxane surfactants can be outstanding wetting agents [11]. As an example, an anionic silicone sulfonate is chosen but polyether trisiloxanes also have frequently been used as wetting agents.

At this point, there is an opportunity to make a comparison with organic surfactants to show interesting structural parallels. Good wetting agents are distinguished by relatively low molecular weight and a strongly branched hydrophobic radical that shows little tendency of crystalline interactions. A typical example of a wetting agent is diisooctyl sulfosuccinate. The trisiloxane radical is structurally comparable to a strongly branched alkyl radical and tends even less towards crystalline interactions. In addition, one can achieve markedly lower surface tensions with silicone surfactants. With trisiloxane sulfonate it is possible to lower the surface tension of water to about 20 mN/m. Polyether trisiloxanes are used, for example, in agrochemical applications to achieve better spreading of aqueous pesticide preparations.
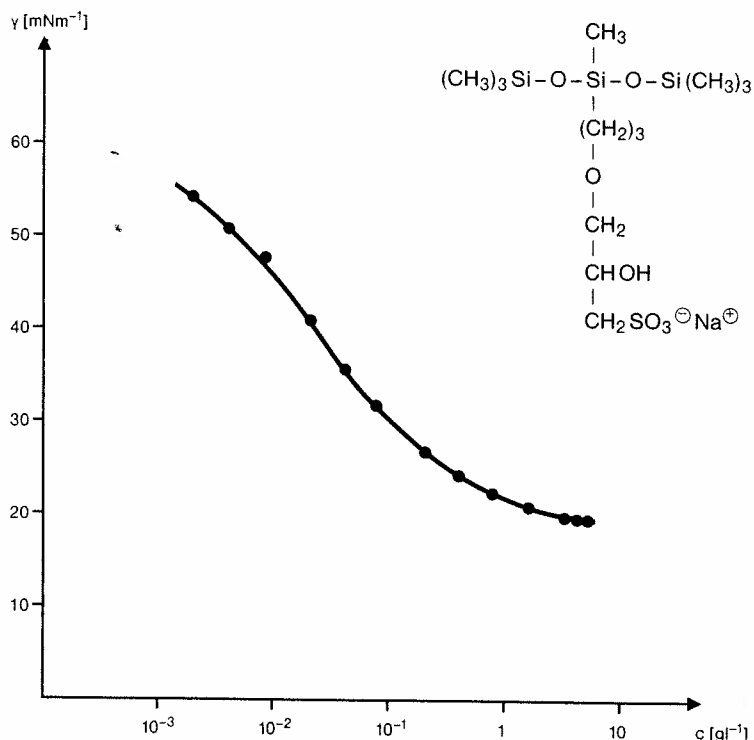
Fig. 10: Surface tension of a trisiloxanes sulfonate in water

Trisiloxane surfactants are not stable against hydrolysis in aqueous solution. This is particularly valid for pH-values outside the range from 7 to 9. Inside this range, however, they can certainly be used in aqueous solutions. Hydrolysis takes place not at the junction to the modifying group but within the trisiloxane radical itself. The process of such a hydrolysis is shown in Fig. 11. Depending on conditions and time, the reaction proceeds more or less completely. This finding may surprise those who visualize the chemical stability of a silicone oil, i.e., of a polydimethylsiloxane.

Summary

Finally, the essential characteristics of silicone surfactants are summarized once again. In the first place, one should name the outstanding surface activity of these products not only in water but also in organic media. In our opinion, this surface activity is achieved to a large extent by the equilibration reaction which allows production of lyophobic blocks of reproducible molecular weight and thus leads to a desired incompatibility. On the other hand, it is just as important to suppress the formation of troublesome sideproducts particularly for critical applications, such as polyurethane foam stabilization. These impurities could be, unmodified or inadequately modified fractions. The key which makes it possible to adapt silicone surfactants to various requirements in a tailor-made manner is found in the possibilities offered by the chemistry of silicone surfactants.
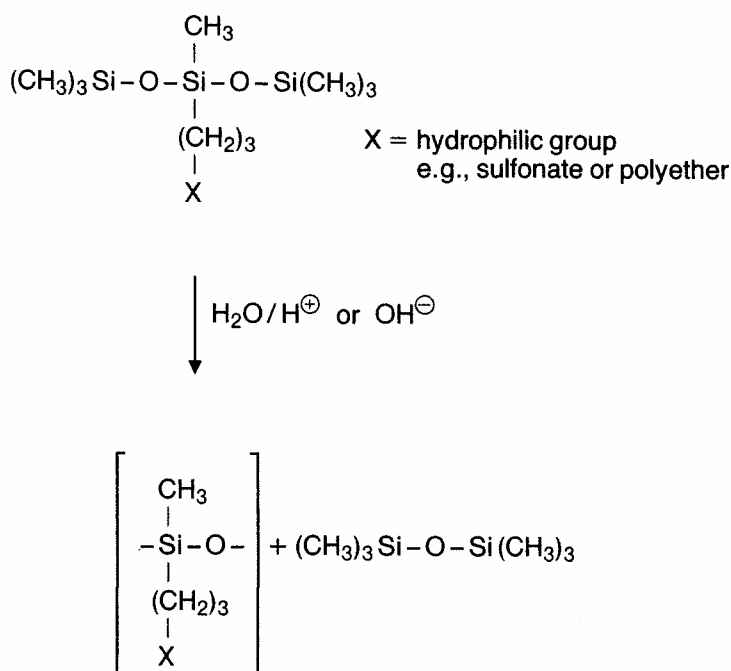
Fig. 11: Hydrolysis of a trisiloxane surfactant

Thus, it is important that

- the fundamental functional lyophobic polymer building blocks can be reproducibly produced with respect to their molecular weight and their molecular-weight distribution,

  as permitted by the equilibration reaction,

- and that these building blocks can be produced with the desired structure and supplied with the desired functionality,

  as permitted by the equilibration reaction, also, and

- finally, that it is possible to introduce the functional groups almost quantitatively into the molecule.

As a result of these facts, a great number of different products becomes feasible which, similar to a building-block system, can be adapted to various requirements. However, one should not conceal the fact that a great deal of experience and knowledge is necessary to utilize these possibilities on a technological scale.

Bibliography

[1] Lammerting, H., R.D. Langenhagen, G. Rossmy and P. Zäske, Goldschmidt AG, DEPS 2 533 074
[2] Ross, S. and G. Nishioka, Colloid and Polymer Sci. 255, 560 (1977)
[3] Noll, W., Chemie und Technologie der Silicone, Verlag Chemie, Weinheim (1968)
[4] Kollmeier, H.J. and R.D. Langenhagen, ,,Goldschmidt informiert..." Heft 63, 41 (1984)
[5] Reid, W.G., Union Carbide Corp., USPS 3 389 160
[6] Hoffmann, K., K.H. Kollmeier and R.D. Langenhagen, Th. Goldschmidt AG, DEPS 3 417 912
[7] Kanner, B., R.A. Pike and H. Mass, Union Carbide Corp., USPS 3 507 897
[8] Grüning, B., U. Holtschmidt and G. Koerner, Th. Goldschmidt AG, DEPS 3 382 881
[9] Rossmy, G., H.J. Kollmeier, W. Lidy, H. Schator and M. Wiemann, ,,Goldschmidt informiert..." Heft 58, 2 (1983)
[10] Wolfes, W., Parfümerie und Kosmetik 68, 195 (1987)
[11] Vick, S.C., Soap/Cosmetics/Chemical Specialities May 1984, 36

Index