Experiments with Light-Induced Oxidative Degradation of Silicones in the Aqueous Phase

by K. Hochgeschwender

1. Aim and purpose of the investigations

The term silicones comprises a multitude of technical products whose property-controlling components are polyorganosiloxanes. Polydimethylsiloxanes, consisting of linear or cyclic siloxane units, represent the major portion of commercially available silicones. This class of substances is described by the formula given in Fig. 1. Because of their molecular structure, siloxanes assume an intermediate position between anorganic and organic compounds, in particular, between silicates and organic polymers [1].

$$X-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{Si}}-O\left[\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{Si}}-O\right]_n\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{Si}}-X, \qquad \left[-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{Si}}-O\right]_n$$

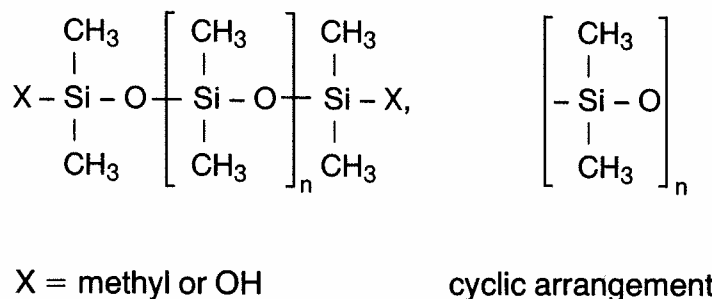$$X = \text{methyl or OH} \qquad \text{cyclic arrangement}$$

Fig. 1: Siloxanes

Methylsiloxanes, because of the chemical stability associated with their structure and desired properties, are considered impossible or at least difficult to be degraded in the environment. In particular, biological degradation of Si-C bonds seems difficult. Only the studies by Heinen [2] indicate the possibility of such a degradation.

In a 1978 lecture, Frye [3] demonstrated for the first time a nonbiological degradation of silicones. He postulated decomposition into oligomer and low-molecular units under certain conditions as the most important method of reduction. The low-molecular compounds, which exhibit a substantially volatility or solubility in water depending on their structure, then are more amenable to degradation reactions.

Abe et al. [5] reported on photolysis of volatile cyclic oligomers, such as gaseous octamethylcyclotetrasiloxane in the presence of ozone. The observed effects indicate a reaction with hydroxy-radicals which are formed from water in the presence of ozone.

In consequence of their structure, methylsilicones are characterized by high chemical stability in the environment. This desired stability makes degradation difficult or impossible.

Hydroxy-radicals also are oxidizing species for demethylation of dimethylsilanediol in nitrate- or nitrite-containing water as was observed by Buch et al. [6]. He observed degradation down to silicic acid. Russi [7] and Kotzias et al. [8] also reported acceleration of the photolysis of organic compounds in water with added nitrate.

Hydroxy-radicals are formed by light exposure of nitrate- and nitrite-ions according to the reactions shown in Fig. 2. Since nitrate- and nitrite-ions have absorption maxima within the range of sunlight (wavelengths above 295 nm), formation of hydroxy-radicals is possible also under environmental conditions [9, 10].

$$NO_3^- + hv + H_2O = NO_2 + OH^- + \cdot OH$$

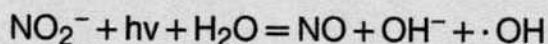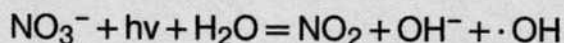$$NO_2^- + hv + H_2O = NO + OH^- + \cdot OH$$

Fig. 2: Formation of hydroxy-radicals

The aim of the research reported in the following was to investigate the light-induced degradation of oligomer and polymer methylsiloxanes in water in the presence of nitrate-ion. For this purpose, a partially water-soluble obligomer mixture (Si 200), consisting of OH-functional dimethylsiloxane chains and cyclic polydimethylsiloxanes, was investigated as well as a linear trimethylsilyl-ended polydimethylsiloxane with an average chain length of 50 dimethylsiloxy-units (" M 50").

2. Exposure requirements

Samples were irradiated in the sun-test apparatus "Original Hanau" with a xenon lamp (NXe 1500, 1.1 kW). The spectral-energy distribution of the lamp is shown in Fig. 3, and the bottom surface of the apparatus was cooled with water to 15°C.

Flat quartz illuminating vessels were filled with 10 ml each of the above-described nitrate-containing solution of Si 200. The vessels were closed with ground stoppers and exposed to light. An equal number of vessels were filled in the same manner and stored in the dark at room temperature. The samples containing polydimethylsiloxane ("M 50") were treated in the same manner.

3. Methods of analysis

Extraction and analysis by atomic absorption spectroscopy (AAS)

The AAS determination of siloxanes rests on measuring the silicon content of the test solution. With regard to these measurements, no distinction is possible between
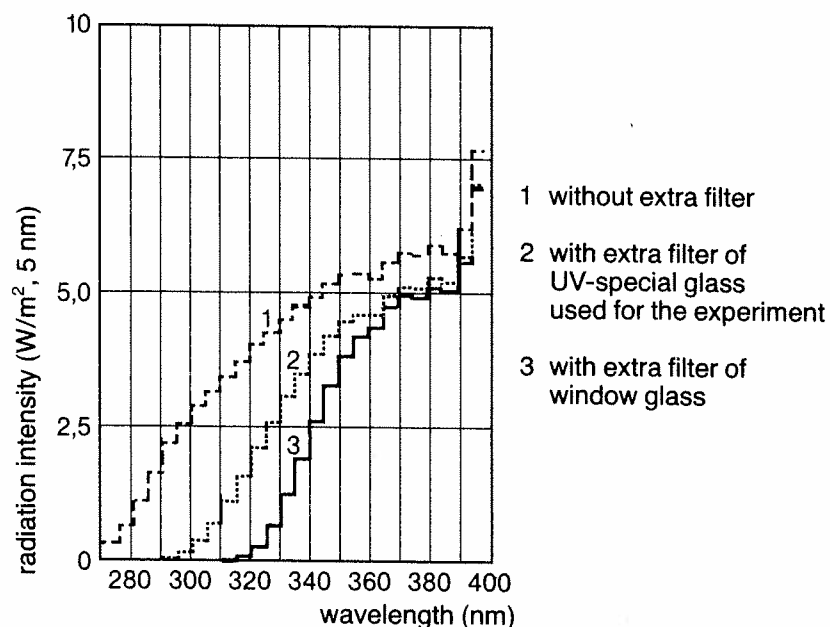
Fig. 3: Xenon lamp ("suntest")

anorganic and organic silicone compounds. Only extraction offers the possibility of separating the two kinds of substances. If one extracts a diluted solution or emulsion of a siloxane mixture with a methylisobutylketone (MIBK)/n-pentanol mixture, the hydrophobic siloxanes are extracted with very high efficiency. To collect also the water-soluble silicone constituents, NaCl is added to the aqueous test solution.

Test procedure

Two samples were exposed to light and two were kept in the dark. After 0, 3, 7, 10 and 17 days, they were kept for one hour under equal conditions for temperature equalization. The contents of the vessels then were stirred for 5 minutes with an extraction mixture (MIBK and pentanol) to which 2 g sodium chloride had been added. After centrifuging, the organic phase was removed and extraction repeated. The Si content of the combined organic phase was determined directly by flame — AAS with a laughing gas-acetylene flame. A MIBK/pentanol solution of known Si 200 content was used for calibration in the concentration range of 5—100 mg Si 200 per liter which is typical for the required measurements. A zerotest for the reagents yielded less than 1 mg "Si 200"/l.

Photometric determination of silicate

The formed silicate was determined by spectrophotometry using the siliconmolybdenum blue reaction which is based on the reduction of silicon molybdate by ascorbic acid.

Exposure in D₂O (NMR analysis)

A specially cleaned 10-ml tubular retort was filled with 1 mg $NaNO_3$, 5 ml highly purified D_2O (MSD isotopes, 99.96 atom-% D) and 1 µl Si 200.

4. Tested substance

As prototype for our investigations, we selected Si 200 which is a mixture of short-chained dimethylsiloxanes with a chain length n = 2 to 15; it contains linear oligomers ending with OH-groups and cyclic oligomers. Preliminary experiments indicated rather low solubility of Si 200 in pure water. Apparently most of the short-chained molecules go into solution, while the less water-soluble cyclic and higher-molecular parts are emulsified or easily evaporated. A method was developed to separate the water-insoluble parts of Si 200 by which a surface film was removed which contained the insoluble constituents of Si 200. After adding 100 µl Si 200 per liter of highly purified water, we obtained solutions in this manner which contained about 20 mg/l water-soluble extractable parts of the Si 200 that were stable over periods of weeks.

For closer characterization of the aqueous Si 200 solution, the latter was extracted with methylenchloride and analyzed for its molar mass distribution by gel chromatography. We found a distribution of about 95% of 250−700 g/mol and about 5% greater than 700 g/mol. The range from 250 to 700 corresponds formally to the compounds $HO[(CH_3)_2SiO]_nH$ where n is between 3 and 9. Highly polar parts of Si 200 are not extractable.

5. Results of decomposition experiments with subsequent determination of siloxane by AAS

The Si 200 content of the aqueous test solution was determined after extraction with a mixture of methyl isobutyl ketone and n-pentanol by means of AAS. This method of analysis covers all siloxanes which can be extracted from water with the mentioned mixture. For a single extraction, the yield was 75 ± 5%.

To create conditions corresponding to the environment, the UV-fraction of the xenon lamp below 290 nm was removed by an duranglass filter. Furthermore, the nitrate concentration was adjusted to 50 mg/l according to the EG-drinking-water regulations. In the environment, the concentration often is lower. Two separate experiments with 10 solutions each were exposed to light under these conditions and 10 solutions were kept in the dark under otherwise as much as possible identical conditions. In intervals of 3−4 days, 2 exposed and 2 unexposed solutions were extracted and the extracts examined with AAS. As can be seen in Fig. 4, the values for the unexposed solutions remained constant, while the exposed solutions clearly indicated decreasing concentrations with increasing exposure duration. Under the assumption of pseudo first-order kinetics, the two experiments indicated a half-life of 9 and 4 days, respectively. The linear relationship of the log concentration with time is shown in Fig. 5 for the first experiment.

exposure time (days)	1st experiment* mg Si 200/l		2nd experiment* mg Si 200/l	
	exposed	unexposed	exposed	unexposed
0		27.5		22.6
2.9	20.2	25.3		
4.0			14.7	22.6
6.9	15.8	25.5		
7.0			9.4	20.9
9.9	11.0	24.7		
11.0			3.4	22.1
13.9	3.0	24.0		
14.0			1.9	20.0
16.9	7.2	25.8		
18.0			1.0	18.8

* = mean for two samples

Fig. 4: Concentration of extractable silicones in aqueous solutions of "Si 200" with exposure in the presence of nitrate
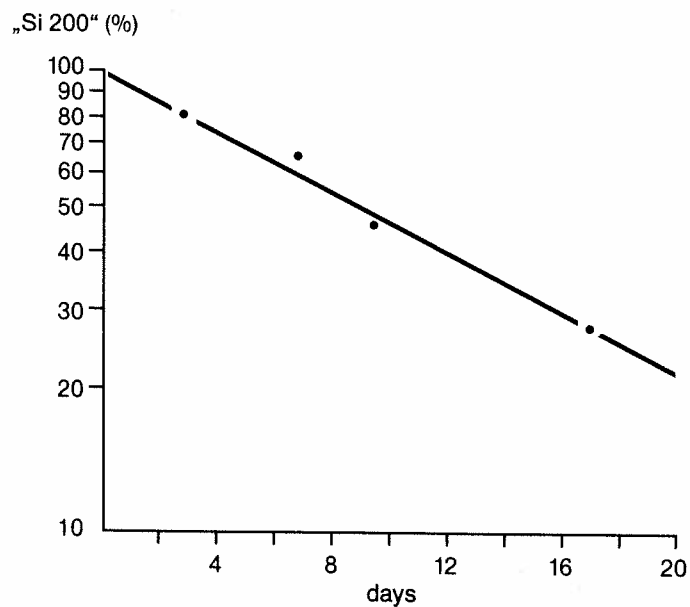

Fig. 5: Photodegradation of "Si 200" in aqueous solution; initial concentration: 27.5 mg "Si 200/l" and 50 mg NO_3^-/l

concentration of extractable silicones: 18 mg/l
computed concentration based on the assumption of a
75% yield: 24 mg/l

exposure time (days)	Si in the form of silicate mg/l**	SiO$_2$* mg/l	−Si(CH$_3$)$_2$O−*
0	< 0.5	< 1.0	< 1.3
8	1.95	4.1	5.1
14	5.65	12.1	14.9
21	7.45	15.9	19.7
35	8.35	17.9	22.0

all unexposed samples contained less than 0.5 mg/l Si as silicate

* computed from the analytical results in column 2
** average of solutions in two sample vessels

Fig. 6: Silicate formation from exposure to light of nitrate-containing, aqueos solutions of "Si 200"

6. Results of degradation experiments with subsequent silicate determination

Formation of silicate from Si 200 by exposure to light in nitrate-containing aqueous solutions was investigated in comparison with unexposed samples also. In one test with a solution of Si 200, that contained 18 mg/l extractable siloxane and 50 mg NO$_3^-$/l, rapid formation of SiO$_2$ was found which after 35 days corresponded to about 90% of the initial amount of siloxane. Results of these experiments are shown in the table in Fig. 6. On the basis of an extraction yield of 75%, the original concentration in the dilute solution was computed to be 24 mg/l. All samples that had been stored in darkness contained less than 0.5 mg silicone in the form of silicate per liter. Evidently, the highly polar, non-extractable, parts of Si 200 are also degraded to silicate by OH-radicals. Silicate determination was performed with the above-mentioned method.

7. Results of degradation experiments in D$_2$O with subsequent analysis by proton-NMR-spectroscopy

In complimentary experiments, Si 200 in D$_2$O was exposed to light in the presence of nitrate ions, and, after adding an internal standard, the concentration of the Si-CH$_3$ groups was determined by FT-proton nuclear resonance spectroscopy. Samples of Si 200 and nitrate in D$_2$O, in two specimen tubes transparent to UV-B light, were exposed to the light from a xenon lamp. Two tubes with identical contents were stored in the dark. After seven days, an internal standard (dioxane in D$_2$O) was added to all samples which were then analyzed by NMR. The analysis of the unexposed solution indicated reproducibly a multiplet of Si-CH$_3$-protons. After exposure, the splitting pattern was clearly changed:
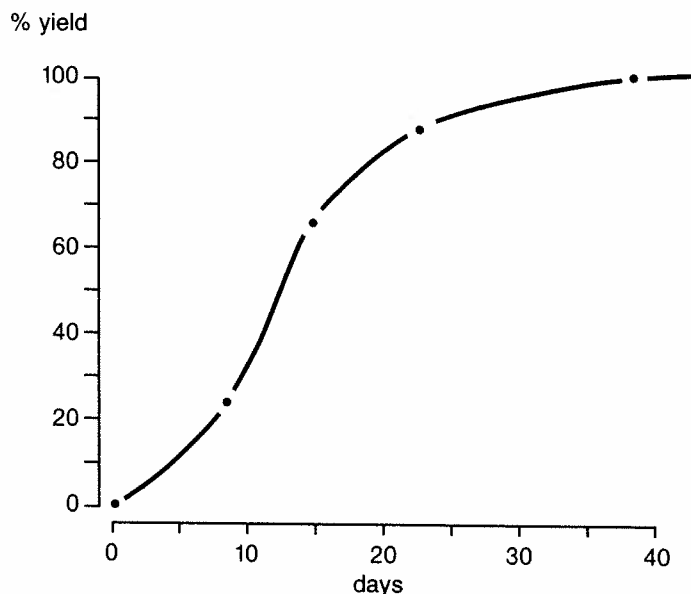
% yield

Fig. 7: Light-induced formation of silicate from "Si 200"

two multiplet peaks were missing. Moreover, exposure significantly reduced the relation of the Si-CH_3-protons to the signal of the internal standard. This means that exposure significantly decreases the concentration of Si-CH_3-groups.

Proton nuclear resonance spectroscopy indicated further that no new signals originated whose area is equivalent to the concentration decrease of the Si-CH_3 signals. Therefore, one can conclude that oxidation to CO_2 was complete. The NMR signals of methyl protons of Si 200 before and after exposure are shown in Fig. 8. These experiments confirmed qualitatively by an independent method the above-described decomposition of siloxane.

8. Experiments with higher-molecular polydimethylsiloxane

To investigate the decomposition of water-insoluble siloxanes, an emulsion was exposed to light that consisted of 1 µl polydimethylsiloxane ("M 50") in 10 ml of highly purified water to which 50 mg/l of nitrate had been added. We used technically pure silicone oil with a viscosity of 50 mm^2s^{-1} at 25°C. Subsequently, the silicate determination was carried out as described in the foregoing. After 37 days, we observed that the amount of silicate corresponded to 1.7% of the initial amount of polydimethylsiloxane while the content of the unexposed sample was well below the detectable limit.

As expected, formation of silicate from higher-molecular weight polydimethylsiloxane proceeded very slowly compared with that for Si 200. This is understandable if one assumes that, because of the very low solubility of polydimethylsiloxane, only a mono-molecular surface layer of the polymer can react with the hydroxy-radicals that are formed

Exposed   Unexposed

$$\frac{Si(CH_3)}{int.\ Std.^*} = 0,10 \qquad \frac{Si(CH_3)}{int.\ Std.^*} = 0,23$$
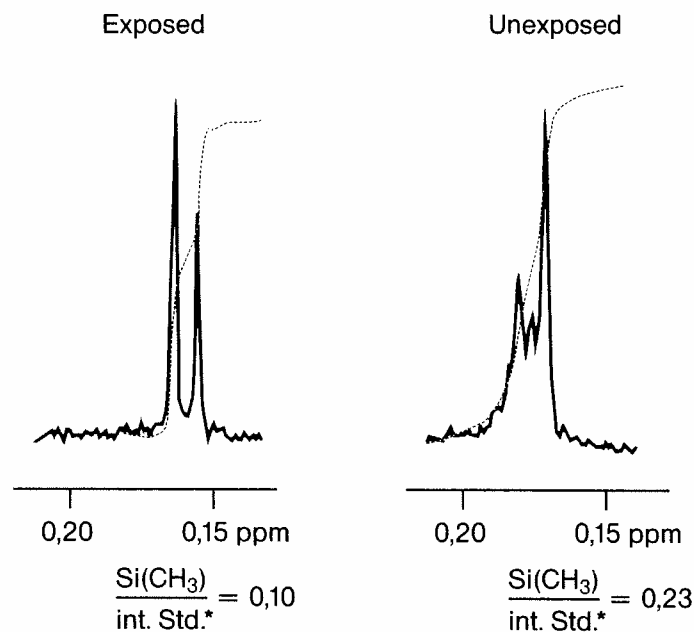
* int. std = internal standard (dioxane)

Fig. 8: Section of the proton — NMR spectra of "Si 200" in D_2O

in the water. Because of the relatively small exposure vessels used for the experiments, one should expect predominantly droplet formation which results in a very small siloxane-water interface.

9. Conclusions

Methylsiloxanes are remarkable because of their stability even at elevated temperatures. As a result, they are considered "persistent". Persistence means durability and stability of chemical materials under environmental influence. The concept of persistence itself is value-free. However, it was used first in connection with certain chlorinated hydrocarbons (for example, DDT) and thereby has acquired a negative connotation. According to Korte [11], persistence is quite generally the stability of organic chemicals in the environment. In principle, one should not consider decomposition of materials as positive and persistence as negative. One should rather distinguish between desirable and undesirable persistence. Materials, such as construction materials, should be stable for the duration of their use. This may be called desirable persistence. If chemicals remain in the environment without change, one speaks of undesirable persistence.

The present experimental results indicate that polydimethylsiloxanes in aqueous solutions are abiotically degradable. In the presence of nitrate ions which can be found in various concentrations in the environment [12], short-chained siloxanes are degraded to silicates by the action of light within days.

Higher-molecular polydimethylsiloxanes also undergo this degradation; however their decomposition proceeds markedly slower under the experimental conditions. It is known that polymer siloxanes in a natural environment are degraded to short-chained fragments [4]. These then are again subject to the here-described light-induced degradation to silicates.

Acknowledgement

Summary

Exposure of aqueous solutions of a mixture of oligomer siloxanes with artificial sunlight in the presence of nitrate ions led to a decrease of the siloxane concentration. Proof was obtained by atom absorption spectroscopy and proton nuclear resonance spectroscopy. Two separate experiments, extraction of the dilute solutions and analysis by AAS, indicated half-lifetimes of 9 and 4 days, respectively. Photolysis of these water-soluble siloxanes yielded silicates as end products. Photometric determination of silicate indicated an almost complete transformation of the initially present siloxanes after 35 days.

Exposure of a dilute emulsion of higher-molecular polydimethylsiloxanes ("M 50") in the presence of nitrate ions, indicated, after 5 weeks under similar experimental conditions, silicate formation that corresponded to 1.7 % of the initial amount of polydimethylsiloxane.

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      Anderson, C., K. Hochgeschwender, H. Weidemann and R. Wilmes: Chemosphere 16 (1987) 2567−2577

Chemistry and Technology of Room-Temperature-Vulcanizable Silicone Rubber

by W. Hechtl

During the 1950's sufficient know-how about room-temperature vulcanization of silicone rubber was obtained that the first commercial products could be sold. At first, these were two-and multi-component systems followed by single-component products.

Numerous areas of applications opened up and Figs. 1 and 2 list examples which particularly clearly indicate the potential of room-temperature-vulcanizable silicone rubber for the solution of many users' problems.

The success of this class of products rests essentially on the combination of two factors: simple processing of the starting materials and extraordinary features of the vulcanized products.

Processing (Figs. 3 and 4):
The room-temperature-vulcanizable single-component silicone rubbers (RTV-1 silicone rubbers) are ready-for-curing compounds which are liquid or have the consistency of a soft paste and react with amospheric humidity to form a silicone elastomer. They are

1. sealants for building construction, glass and window construction and sanitary use

2. universally applicable and ready-to-use adhesive for seals, joints and coatings

3. heat- and cold-resistant adhesives for metals, glass, ceramics and synthetic materials

4. on-the-spot production of seals

5. static seals FIPG (formed in place gasket) for automobile manufacture

6. sealing of steam chamber for flat irons

7. cementing and attaching of pipes and television tubes

Fig. 1: Examples for applications of RTV-1 silicone rubbers (RTV-1 = room-temperature-vulcanizable, single-component)

1. sealing and encapsulating of electrical and electronic elements; also gels for vibration damping

2. elastic damping elements

3. production of prefabricated cable terminations

4. roll coverings for electrographic instruments

5. production of embossing stamps and flexible pads for transfer printing

6. flexible molds for the porcelain industry, for making plaster moulds

7. flexible molds for publicity gifts, for the reproduction of handicraft articles, decorative furniture parts and prototypes

8. mold making materials for dentists, ear-specialists and orthopaedic surgeons

9. bonding of solar cells for satellites

Fig. 2: Examples for applications of RTV-2 silicone rubbers (RTV-2 = room-temperature-vulcanizable, two components)

1. ready-to-use materials that are pourable or have the consistency of a soft paste

2. containers: tubes, cartridges, barrels

3. application: by hand, hand or pneumatic pistol, automatic extrusion and metering devices

4. vulcanization by contact with atmospheric humidity

Fig. 3: Processing of RTV-1 silicone rubber

1. pourable, spreadable, kneadable materials

2. mixing of pourable and spreadable components with mechanical stirrer or spatula; kneadable rubbers are mixed by hand, on the rolls or in an internal mixer

3. use of mixing and metering devices

4. vulcanization is strongly accelerated by elevated temperatures for addition-curing RTV-2 types

Fig. 4: Processing of RTV-2 silicone rubber

sold in tubes, cartridges or barrels and can be applied by hand or machine. Cartridges are used with either hand- or pneumatic pistols. Larger jobs are performed mostly with automatic extrusion and metering devices. As already mentioned, RTV-1 silicone rubbers need atmospheric humidity for vulcanization. In the course of cure a more or less volatile product is released.

Room-temperature-vulcanizable two-component silicone rubbers (RTV-2 silicone rubbers) are pourable, spreadable and kneadable compounds which cure after addition of the second component and form an elastomer. Uniform mixing of the material and the catalyst can be achieved with a spatula or a mechanical stirrer if the compound is pourable or spreadable. For work with larger quantities, it is recommended to use a mixing and metering device; use of static mixing tubes has been found particularly valuable. For the addition-curing RTV-2 types, one often utilizes strongly accelerated vulcanization at elevated temperatures.

The properties of the vulcanized end product essentially do not depend on whether it was formed from a room-temperature vulvanized one- or two-component rubber (Fig. 5). Primarily, one must mention: retention of the rubber elasticity even under severe conditions, such as heat, cold and environmental exposure. The electrical properties are comparable to those of other insulating materials, but one should point out the difference in low temperature dependence.

Next, one should mention the release properties of the surface towards anorganic and organic materials; at the same time, one can achieve adhesion to most substrates − at least after preliminary treatment with a suitable primer. Finally, one should point to the good chemical stability with respect to weak acids and alkalis as well as to salt solutions. Solvents cause more or less pronounced swelling which however is largely reversible. For special types, such as the fluorosilicone elastomers swelling by nonpolar agents is greatly reduced.

Important properties of the vulcanizate

1. continuance of elasticity under stress by heat, weather and radiation

2. electric insulation properties

3. release properties

4. adhesion to many substrates

5. chemical stability

Fig. 5: RTV-1 and RTV-2 silicone rubber

The formulations of RTV-1 and RTV-2 silicone rubbers include silicone polymers, cross-linking agents, cross-linking catalysts and primarily fillers as well as special additives (Fig. 6). Processing and vulcanization characteristics are determined by the combination of silicone polymers/cross-linking agents and cross-linking catalyst; mechanical properties depend on the combination of silicone polymers and fillers. Special additives serve to achieve particular effects or improvements of some property.

Composition

1. Silicone polymer

2. fillers

3. cross-linking agent and catalyst

4. special additives

Fig. 6: RTV-1 and RTV-2 silicone rubber

$$
\underset{\underset{Me}{|}}{\overset{\overset{Me}{|}}{HO-Si}}-O-\underset{\underset{Me}{|}}{\overset{\overset{Me}{|}}{Si}}-\left[\underset{\underset{Me}{|}}{\overset{\overset{Me}{|}}{O-Si}}\right]_{x}-O-\underset{\underset{Me}{|}}{\overset{\overset{Me}{|}}{Si}}-O-\underset{\underset{Me}{|}}{\overset{\overset{Me}{|}}{Si}}-OH
$$

or

$$
CH_2=CH-\underset{\underset{Me}{|}}{\overset{\overset{Me}{|}}{Si}}-O-\underset{\underset{Me}{|}}{\overset{\overset{Me}{|}}{Si}}-\left[\underset{\underset{Me}{|}}{\overset{\overset{Me}{|}}{O-Si}}\right]_{x}-O-\underset{\underset{Me}{|}}{\overset{\overset{Me}{|}}{Si}}-O-\underset{\underset{Me}{|}}{\overset{\overset{Me}{|}}{Si}}-CH=CH_2
$$
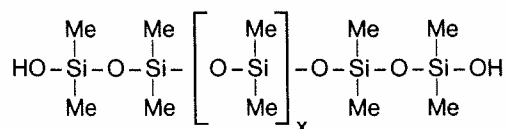
$Me = CH_3$
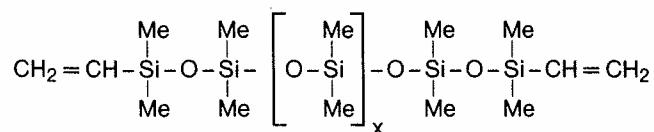
x in the range 200–2,000

Fig. 7: Silicone polymers for RTV-1 and RTV-2 silicone rubber

The usual silicone polymers are linear dimethylpolysiloxanes having as end groups either hydroxyl- or vinyl groups (Fig. 7). Polymers which are endblocked with hydroxyl groups are produced either from cyclic dimethylsiloxanes or by polycondensation of short-chained hydroxyl-terminated dimethylsiloxanes which themselves are formed by hydrolysis of dimethyldichlorosilane.

Production of vinyl end-blocked polymers requires special measures to achieve quantitative end-blocking.

During cross-linking, only the functional groups of the silicone polymer react, that is, the hydroxyl- or the vinyl-end groups. This means that the cross-link density is determined by the concentration of these functional groups or by the average chain length of the used silicone polymer, more precisely, its molecular-weight distribution. Since the cross-link density has a decisive influence on the stress-strain characteristics, one can control the elastic modulus of RTV-1 and RTV-2 rubber by the chain length of the silicone polymer, typically in the range between 200 and 2000 siloxane chain groups.

The definite cross-linking reaction under exclusive use of functional polymer end groups is in contrast to many cross-linking reactions by radicals, for example, peroxide cross-linking of heat-vulcanized silicone rubbers, for which all methyl groups of the dimethyl-polysiloxane are available as potential cross-linking sites. For this reason, room-temperature-vulcanized silicone rubbers are frequently used as model networks to compare experimental data with a mathematical description based on a theory of the elastic behavior.
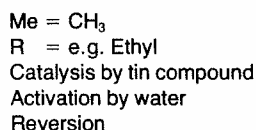
Another essential aspect is that the silicone polymer network contributes unfortunately only to a small degree to the mechanical strength of room-temperature-vulcanized silicone rubbers although this property is important for most applications. Interaction

Composition	Dimethylpolysiloxane no filler	Mixture of dimethylpolysiloxane and a reinforcing filler
viscosity [mPa · s]	20,000	20,000
hardness Shore A (DIN 53 505)	23	23
tensile strength [N/mm^2] (DIN 53 504, S 3 A)	0.5	6.0
tear resistance [N/mm] (ASTM D 624 B)	not measureable	25

Fig. 8: Effect of reinforcing filler on the mechanical properties

between dimethylsiloxane chains is quite weak which is apparent from the low glass transition temperature of $-123°C$ and the very high permeability for gases. The necessary and successful approach in this situation is addition of fillers, whereby the mechanical strength of the vulcanizate is related to the surface and nature of the particular filler material. Fumed silica has been found in many cases to be almost indispensible, and types with a specific surface between 150 and 300 m^2/g are most commonly used. On the surface, there are silicon-bonded hydroxyl-groups that interact with the siloxane groups of the polymer chains through hydrogen bonds and in this manner create a "mechanical reinforcement". Values of the tensile strength and tear resistance that can be achieved by application of a reinforcing filler are shown in Fig. 8. It is astonishing in this example that initial viscosity and durometer hardness can be kept low. This is at first amazing because one would expect that a reinforcing filler would increase both viscosity and durometer hardness. However, these surprising results can be achieved by suitable formulation of the compound and control of the siloxane cross-link density.

Condensation-curing RTV-2 rubbers were the first products sold as room-temperature-vulcanizable silicone rubbers. Figure 9 shows the cross-linking principle. The hydroxyl end groups of the dimethylpolysiloxane react with a silicic-acid ester, e.g., tetraethyl-silicate, by condensation and release of an alcohol, e.g., ethyl alcohol. The reaction is catalyzed with a tin catalyst, such as dibutyltindilaurate. To achieve rapid and reproducible deep-layer vulcanization, one most provide for a water content in the parts-per-thousand range which comes mostly from the moisture in the mixed-in filler without special measures. The alcohol released during cross-linking must be removed to achieve the final properties of the vulcanizate which means that a surface layer open to air is necessary. If vulcanization takes place in a closed system, the danger exists that subsequent heating will result in refluidization by a reversal reaction of the alcohol with the siloxane cross-links. This process is called reversion and can be avoided by using special cross-linking

$$4 \ -O-\underset{\underset{Me}{|}}{\overset{\overset{Me}{|}}{Si}}-O-\underset{\underset{Me}{|}}{\overset{\overset{Me}{|}}{Si}}-OH + RO-\underset{\underset{OR}{|}}{\overset{\overset{OR}{|}}{Si}}-OR \ \rightleftharpoons$$

Fig. 9: Condensation-curing RTV-2 silicone rubber — cross-linking principle

+ 4 ROH

Me = CH₃
R = e.g. Ethyl
Catalysis by tin compound
Activation by water
Reversion

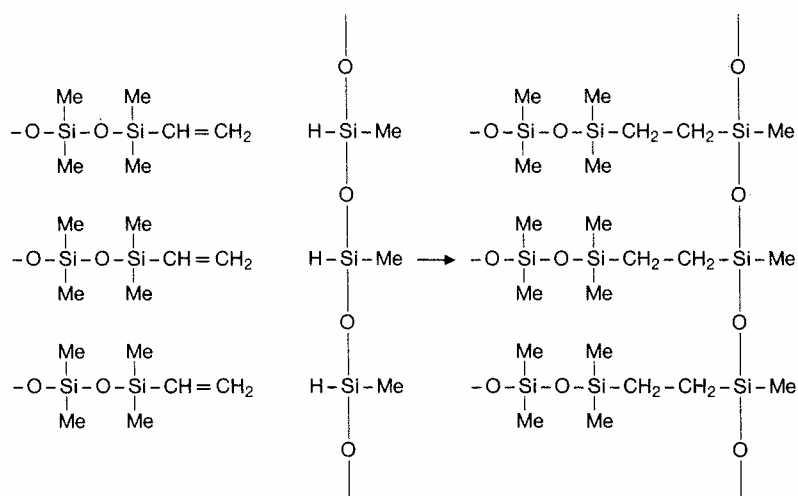Fig. 9: Condensation-curing RTV-2 silicone rubber — cross-linking principle

catalysts and fillers. Condensation curing is naturally associated with shrinkage. Values for linear shrinkage depend on the amount of cross-linking agent and lie between 0.2 and 1.0 %. A mixture of silicic-acid ester and a tin compound serves as second component (usually called "catalyst") whose type and dosage determine the pot life and the time required until the rubber is demoldable (see Fig. 10).

catalyst	pot life 23 °C/50 % rel. humidity	Time until demolding 23 °C/50 % rel. humidity
3 weight % catalyst 1	about 90 mins.	20 − 25 hours
4 weight % catalyst 1	about 80 mins.	5 − 6 hours
2 weight % catalyst 2	about 40 mins.	3.5 − 4 hours
3 weight % catalyst 2	about 20 mins.	1.5 − 2 hours

Molds must be exposed to the atmosphere for about 24 hours/1 cm wall thickness

Fig. 10: Condensation-curing RTV-2 silicone rubber
Processing and time required to remove from mold

$$-O-\underset{\underset{Me}{|}}{\overset{\overset{Me}{|}}{Si}}-O-\underset{\underset{Me}{|}}{\overset{\overset{Me}{|}}{Si}}-CH=CH_2 \qquad H-\underset{\underset{O}{|}}{\overset{\overset{O}{|}}{Si}}-Me \qquad -O-\underset{\underset{Me}{|}}{\overset{\overset{Me}{|}}{Si}}-O-\underset{\underset{Me}{|}}{\overset{\overset{Me}{|}}{Si}}-CH_2-CH_2-\underset{\underset{O}{|}}{\overset{\overset{O}{|}}{Si}}-Me$$

$$-O-\underset{\underset{Me}{|}}{\overset{\overset{Me}{|}}{Si}}-O-\underset{\underset{Me}{|}}{\overset{\overset{Me}{|}}{Si}}-CH=CH_2 \qquad H-\underset{\underset{O}{|}}{\overset{\overset{O}{|}}{Si}}-Me \longrightarrow -O-\underset{\underset{Me}{|}}{\overset{\overset{Me}{|}}{Si}}-O-\underset{\underset{Me}{|}}{\overset{\overset{Me}{|}}{Si}}-CH_2-CH_2-\underset{\underset{O}{|}}{\overset{\overset{O}{|}}{Si}}-Me$$

$$-O-\underset{\underset{Me}{|}}{\overset{\overset{Me}{|}}{Si}}-O-\underset{\underset{Me}{|}}{\overset{\overset{Me}{|}}{Si}}-CH=CH_2 \qquad H-\underset{\underset{O}{|}}{\overset{\overset{O}{|}}{Si}}-Me \qquad -O-\underset{\underset{Me}{|}}{\overset{\overset{Me}{|}}{Si}}-O-\underset{\underset{Me}{|}}{\overset{\overset{Me}{|}}{Si}}-CH_2-CH_2-\underset{\underset{O}{|}}{\overset{\overset{O}{|}}{Si}}-Me$$

$Me = CH_3$
Catalysis by platinum compound
No reversion

Fig. 11: Addition-curing silicone rubber — cross-linking principle

Addition-curing RTV-2 silicone rubbers steadily increase in economic importance. Figure 11 shows the cross-linking principle. The so-called hydrosilation reaction of the vinyl double bond is catalyzed at the desired speed by platinum compounds in the parts-per-million range. Since, in contrast to condensation cross-linking, no low-molecular by-product is formed, it is possible to vulcanize in a closed system with subsequent heating. No reversion takes place, and linear shrinkage is generally below 0.1%. A very important advantage of the addition-curing system is that it is possible to obtain rapid vulcanization by increasing the temperature (see Fig. 12). A drawback of the addition-curing system is that the platinum catalyst can be "poisoned", e.g., by sulfur-, tin- or nitrogen-compounds so that no vulcanization takes place. In the case of contact with other materials, this must be ascertained by preliminary experiments.

The principle of room-temperature-vulcanization of single-component silicone rubbers (RTV-1) was discovered toward the end of the 1950's. As in the case of condensation curing RTV-2 silicone rubber, the hydroxyl end-blocked dimethylpolysiloxane serves as the essential part of the compound. With addition of certain cross-linking agents and cross-linking catalysts, one finds, surprisingly, that vulcanization can at first be prevented if one assures absolutely water-free conditions. This can be achieved, for example, by an excess of cross-linking agent which removes moisture from the system because of its reactivity with water and thus acts as a drying agent. In this manner, RTV-1 silicone rubber is also suitable for long-term storage in moisture-impermeable tubes or cartridges.

pot life at room temperature	60 minutes
time until demolding at room temperature	10 hours
final hardness at room temperature	after 24 hours
final hardness at 50°C	after 1 hour
final hardness at 100°C	after 10 minutes
final hardness at 150°C	after 5 minutes

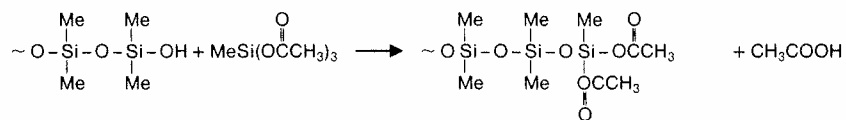hot vulcanization in a convection furnace, thickness of layer = 1 cm

Fig. 12: Addition-curing RTV-2 silicone rubber — vulcanization characteristics

The material squeezed out of its holder for use is subsequently vulcanized under the influence of atmospheric humidity. An example of the oldest RTV-1 system, the so-called acetoxysystem, is shown in Fig. 13 which represents the cross-linking principle. In the first step, the cross-linking agent endblocks the polymer, whereby the already mentioned intermediate product is formed which is stable during storage. Reaction with water then leads to hydrolytic cleavage of the acetoxy-groups and formation of reactive hydroxyl groups. The latter condense with other acetoxy-groups, which can be bonded to the cross-linking agent or to the polymer, with formation of acetic acid. Finally, all acetoxy-groups have reacted and a siloxane network is formed. The cure rate depends on the concentration of available water, that is, the relative atmospheric humidity; furthermore, it is diffusion-controlled and thus dependent on the thickness of the layer. It has become customary in practice to use the term "skin forming time" which means the time in which a nonsticking, elastic surface is formed under standard environmental conditions — for example 23°C/50% relative humidity. As a rule, the skin forming time which is a measure for the workability is adjusted to a range of 10–60 minutes. The time dependence of deep section cure is shown in Fig. 14. With one-sided access of atmosphere, the thickness of the layer should not exceed 1 cm.

Numerous other RTV-1 systems have been developed after the acetoxy-system (see Fig. 15). The last example, the alkoxy-system, indicates the technical progress in the area of RTV silicone rubber. Originally, it was developed as a condensation-curing RTV-2 rubber but can be managed today as a RTV-1 system.

RTV-1 silicone rubbers are nearly universally useful for sealing, cementing and coating. For a successful application it is essential to have a permanent adhesion to whatever substrate is used (Fig.16). To many surfaces RTV-1 caulking and cement materials have sufficient adhesion which satisfies most requirements. However, if the bonded elements are subjected to high loads, such as temperature changes, moisture, tension or shear stress, it is recommended to use a primer. Primers are dilute solutions which contain reactive silanes, silicone resins and condensation catalysts. They are applied to the cleaned surface in a thin layer; after a required drying time, a still-reactive layer of resin
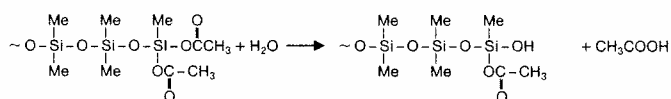
1. water-free conditions
   reaction of cross-linking agent with the hydroxyl end-groups
   of the silicone polymer

$$\sim O-\underset{\underset{Me}{|}}{\overset{\overset{Me}{|}}{Si}}-O-\underset{\underset{Me}{|}}{\overset{\overset{Me}{|}}{Si}}-OH + MeSi(O\overset{O}{\overset{||}{C}}CH_3)_3 \longrightarrow \sim O\,\underset{\underset{Me}{|}}{\overset{\overset{Me}{|}}{Si}}-O-\underset{\underset{Me}{|}}{\overset{\overset{Me}{|}}{Si}}-O\,\underset{\underset{\underset{O}{||}}{\overset{|}{O}CCH_3}}{\overset{\overset{Me}{|}}{Si}}-O\overset{O}{\overset{||}{C}}CH_3 \quad + CH_3COOH$$

Me = CH₃
tin catalyst

Fig. 13 a: RTV-1 silicone rubber acetoxy system — cross-linking principle

2. cross-linking under influence of water
   a) hydrolysis of the polymer-bonded acetoxy-group

$$\sim O-\underset{\underset{Me}{|}}{\overset{\overset{Me}{|}}{Si}}-O-\underset{\underset{Me}{|}}{\overset{\overset{Me}{|}}{Si}}-O-\underset{\underset{\underset{O}{||}}{\overset{|}{O}\overset{|}{C}-CH_3}}{\overset{\overset{Me}{|}}{Si}}-O\overset{O}{\overset{||}{C}}CH_3 + H_2O \longrightarrow \sim O-\underset{\underset{Me}{|}}{\overset{\overset{Me}{|}}{Si}}-O-\underset{\underset{Me}{|}}{\overset{\overset{Me}{|}}{Si}}-O-\underset{\underset{\underset{O}{||}}{\overset{|}{O}\overset{|}{C}-CH_3}}{\overset{\overset{Me}{|}}{Si}}-OH \quad + CH_3COOH$$

b) condensation of the activated hydroxyl end-group with cross-linking agent
   or polymer-bonded acetoxy-group with formation of Si—O—Si, e.g.

$$\sim O-\underset{\underset{Me}{|}}{\overset{\overset{Me}{|}}{Si}}-O-\underset{\underset{Me}{|}}{\overset{\overset{Me}{|}}{Si}}-O-\underset{\underset{\underset{O}{||}}{\overset{|}{O-C-CH_3}}}{\overset{\overset{Me}{|}}{Si}} OH + CH_3-\overset{O}{\overset{||}{C}}-O-\underset{\underset{Me}{|}}{\overset{\overset{Me}{|}}{Si}}-O-\underset{\underset{Me}{|}}{\overset{\overset{Me}{|}}{Si}}-O-\underset{\underset{\underset{O}{||}}{\overset{|}{CH_3-C-O}}}{\overset{\overset{Me}{|}}{Si}}-O \longrightarrow$$

usw.

$$O-\underset{\underset{Me}{|}}{\overset{\overset{Me}{|}}{Si}}-O-\underset{\underset{Me}{|}}{\overset{\overset{Me}{|}}{Si}}-O-\underset{\underset{\underset{CH_3}{|}}{\overset{|}{O=C}}}{\overset{\overset{Me}{|}}{Si}}-O-\underset{\underset{\underset{CH_3}{|}}{\overset{|}{C=O}}}{\overset{\overset{Me}{|}}{Si}}-O-\underset{\underset{Me}{|}}{\overset{\overset{Me}{|}}{Si}}-O-\underset{\underset{Me}{|}}{\overset{\overset{Me}{|}}{Si}}-O \quad + CH_3COOH$$
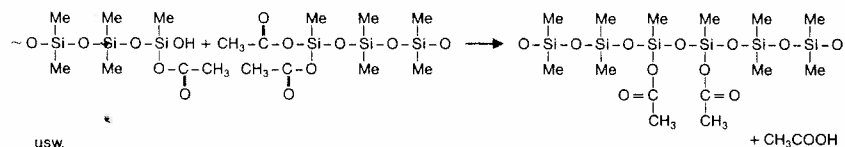
Fig. 13 b: RTV-1 silicone rubber — acetoxy system — cross-linking principle

is formed which evidently can form a chemical bond with the subsequently applied silicone rubber. Unfortunately, there is no universal primer only many special-purpose primers for the various combinations of silicone-rubber types and substrates. Little is known about the necessary reactions on the boundary surface which are essential for achieving bonding; for solving a particularly difficult bonding problem one must rely on experience and trial-and-error. It seems certain that spectroscopic surface analysis will be the future method of choice to shed some light on these bonding processes.

RTV-2 silicone rubber usually does not adhere to the substrate. In most cases, a primer pretreatment is required to achieve secure bonding.

Deep section cure of a 2-cm layer
at 23°C/50% rel. humidity

cure time	depth of cured layer
1 day	0.2 cm
2 days	0.35 cm
3 days	0.5 cm
4 days	0.65 cm
5 days	0.75 cm

Fig. 14: RTV-1 silicone rubber

Designation	Functional Group	Separated Product
acetoxy-	$-O-\overset{\overset{O}{\|\|}}{C}-CH_3$	acetic acid
oxime-	$-O-N=C\overset{\diagup R}{\diagdown R'}$	an oxime
amine-	$-N\overset{\diagup R}{\diagdown R'}$	an amine
amide-	$-\underset{R}{N}-\overset{\overset{O}{\|\|}}{C}-R'$	an amide
aminoxy-	$-O-N\overset{\diagup R}{\diagdown R'}$	a hydroxyl amine
isopropenoxy-	$-O-\underset{CH_3}{C}=CH_2$	acetone
alkoxy-	$-OR$	an alcohol

R = H, alkyl   R′ = alkyl, aryl

Fig. 15: RTV-1 cure systems

RTV-1 silicone rubber

1) usually adequate adhesion

2) pretreatment of the substrate surface with primer
for high loads

RTV-2 silicone rubber

1) usually no adhesion

2) generally pretreatment of the substrate surface
with a primer

Fig. 16: RTV silicone rubber-adhesion

Room-temperature-vulcanizable silicone rubber exhibits a number of unusual properties and therefore offers a solution for many technical problems (Fig. 17). Flexibility at low temperatures is remarkable; vulcanizates whose polymer chains consist exclusively of dimethylsiloxane units are flexible to about -50°C. Replacing the dimethylsiloxane units by phenylmethylsiloxane units or diphenylsiloxane units can lower the stiffening temperature to about -110°C. Correspondingly modified silicone-rubber adhesives have proved themselves for space applications, such as, solar-cell mountings for satellites. Rupture of rigid bonds, which would be caused by dimensional changes under extreme temperature variations, is prevented by the elastic intermediate layer of silicone rubber. This is an indication that no hardening or brittleness is to be feared for outdoor use – such as for building construction.

Furthermore, one must point out the excellent weathering and aging resistance. Vulcanizates of room-temperature-vulcanized silicone rubber change only insignificantly even during weathering exposure over years. A test result of the so-called xenotest 1200 is shown in Fig. 18; here, dry/wet or light/dark periods alternate and the exposure corresponds to outdoor radiation including the UV portion.

One of the prominent properties is temperature stability. At 180°C, most vulcanizates maintain their elasticity practically without limit (see Fig. 19). Heat stabilized types withstand exposures to 250°C for surprisingly long periods (Fig. 20).

The electrical prooperties of vulcanizates of silicone rubber at room temperature are comparable to those of other insulating materials (Fig. 21). It is important however to note that these properties, particularly volume resistivity, dielectric strength and dielectric losses hardly change at higher temperatures. Also, storage in water causes only minor and reversible changes of the electrical properties. The extraordinary tracking resistance and the resistance to corona discharge are to be emphasized, particularly for special types.

1) Polymer chains containing exclusively dimethyl-
   siloxane units:

   flexibility to about $-50°C$

2) Polymer chains containing also phenylmethylsiloxane
   or diphenylsiloxane units:

   flexibility to about $-110°C$

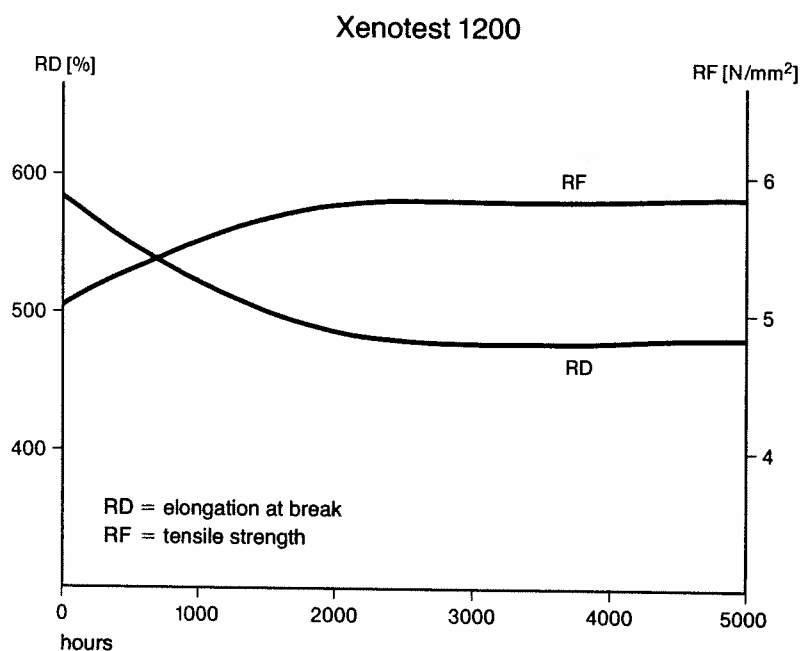Fig. 17: RTV silicone rubber – low-temperature flexibility

Xenotest 1200

Fig. 18: RTV silicone rubber – weatherability
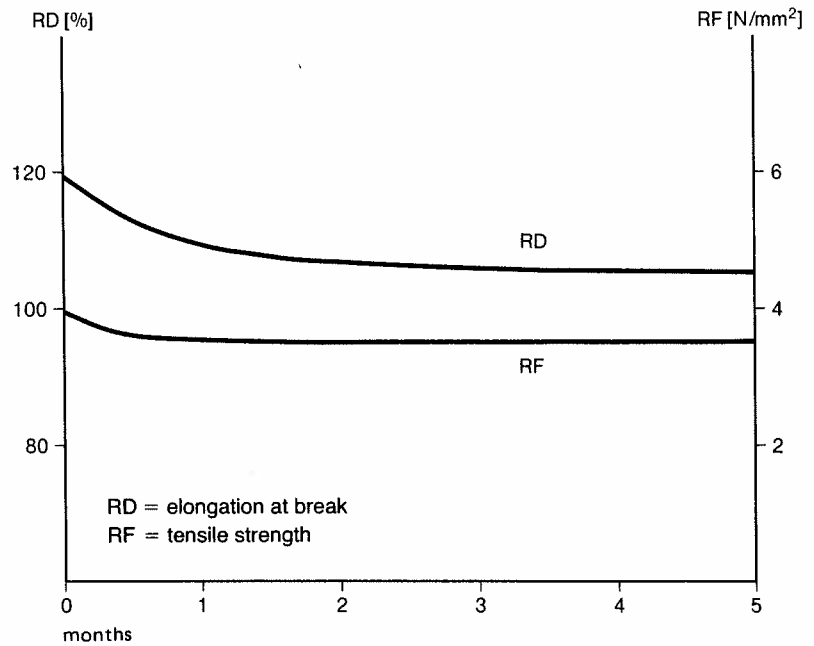
Heat stability at 180°C

RD [%]   RF [N/mm²]

120   6

RD

100   4

RF

80   2

RD = elongation at break
RF = tensile strength

0   1   2   3   4   5
months

Fig. 19: RTV silicone rubber

Heat stability at 250°C

RD [%]   hardness Shore A

300   40

RD

200   30

Shore A

100   20

1   2   3   4   5   6   7   8   9   10   11
months
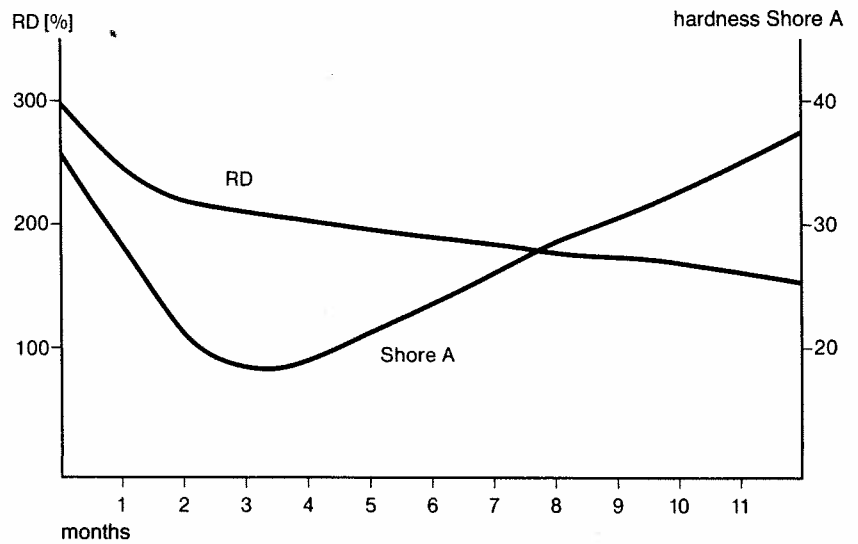
Fig. 20: RTV silicone rubber (heat-stabilized)

dielectric strength (DIN 53481, 1 mm layer thickness)	23	kV/mm
volume resistivity (DIN 53481, measured dry at 23°C)	$1 \cdot 10^{16}$	$\Omega \cdot cm$
surface resistance (DIN 53482)	$5 \cdot 10^{12}$	Ω
dielectric constant (DIN 53483)	at 50 Hz at 5 MHz	3.2 3.0
loss factor tan δ (DIN 53483)	at 50 Hz at 5 MHz	$55 \cdot 10^{-4}$ $30 \cdot 10^{-4}$

Fig. 21: RTV silicone rubber – electric properties

Finally, one should point to the release properties which surfaces of RTV silicone rubbers exhibit toward inorganic or organic materials; this behavior combined with the molding precision are the reasons for the wide-spread use of RTV-2 silicone rubber for producing elastic molds.

In summary, one can say that the properties of RTV silicone rubber are unique in many respects in comparison with those of other elastomers. This and the fact of easy processing assure many possible applications.

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Structure and Properties of Hot-Vulcanized Silicone Rubbers

by D. Wrobel

1. Economic Importance

Hot-vulcanized silicone rubbers have been known for over 45 years but are still of considerable interest. Because of the outstanding properties of articles made of silicone rubber, particularly at higher temperatures, and because of the high potential for innovations, these materials enjoy an above-average growth rate compared with that of many other elastomers. This applies especially to the new group of liquid silicone rubbers. This year, the world market for both materials should reach about 100,000 t or about $^1/_5$ of the total silicone market.

The growth in terms of quantity parallels steady improvements in production technology and an associated decrease in costs. Price differentials between the classic organic rubbers and the silicone rubbers have steadily decreased. At the same time, the mechanical properties of silicone elastomers have gradually approached the level of other synthetic rubbers. Thereby, these silicone materials became economically more and more interesting for technical applications.

2. Chemical Foundations

Of the entire field of silicone elastomers, only the high strength rubbers which are vulcanized at higher temperatures will be considered. These so-called hot-vulcanized silicone rubbers are divided into solid rubbers, which are processed like normal organic rubbers, and liquid silicone rubbers; the latter have been marketed for about 12 years.

Essentially, both materials consist of polydimethylsiloxanes with reactive vinyl groups, surface-modified finely dispersed silica and a suitable cross-linking agent. Furthermore, many types for special applications contain added fillers, hot-air stabilizers, flame retardant materials or pigments. Rubbers with a different basic polymer, e.g., phenyl-silicone rubbers or fluorosilicone rubbers, are used only in special cases.

Polymers

The chain lengths of the polysiloxanes differ according to the rubber group. While solid rubbers require highly viscous and therefore high-molecular polymers for processing, the viscosity of the polysiloxanes for liquid silicone rubbers should be as low as possible. As a rule, strictly linear polymers with molecular weights between 400,000 and 600,000 g/mol are used for solid rubbers. Such polymer with an average of about 6,000 siloxy units are water-clear Newtonian liquids with viscosities of 15,000−30,000 Pa.s.

In contrast to organic polymers of similar molecular weights, the polydimethylsiloxanes have a relatively low viscosity because of their small intermolecular interactions and exhibit Newtonian behaviour at low shear rates ($D = 10^{-2} s^{-1}$).

$$CH_2=CH-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{Si}}-O\left[-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{Si}}-O\right]_n-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{Si}}-CH=CH_2$$

$$R-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{Si}}-O\left[-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{Si}}-O\right]_n\left[-\underset{\underset{CH=CH_2}{|}}{\overset{\overset{CH_3}{|}}{Si}}-O\right]_m-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{Si}}-R$$
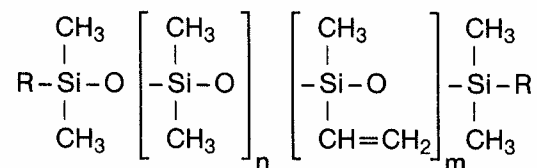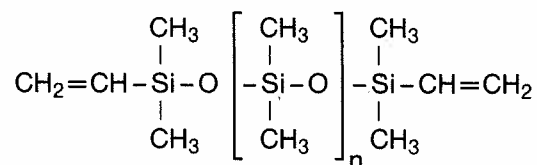
$$R = CH_3, CH=CH_2 \qquad \frac{m}{m+n} \cdot 100 = 1 \text{ to } 10$$

Fig. 1: Polymers for silicone rubbers

The polymers used (see Fig. 1) consist mainly of polydimethylsiloxanes with dimethyl-vinylsiloxy end groups or with a few vinylmethylsiloxy groups in the chain. Beyond that, it has been found that a heterogeneous distribution of the vinyl groups leads to improved tear strengths. Accordingly, rubber types with high tear strengths contain additional vinyl-rich polymers.

Liquid silicone rubbers have, in principle, the same structure as solid rubbers. However, the average chain length of the polymers is lower by a factor of about 6. This is related to a lowering of the viscosity by a factor of 1,000 to 20 – 40 Pa.s. This extreme dependence of the viscosity on chain length is characteristic of all linear polymers. It is not a property unique to polydimethylsiloxanes but is a result of the chain-shaped molecular structure.

Cross-linking

Cross-linking of solid and liquid silicone rubbers to an elastomer can be accomplished either by a peroxidic or an addition reaction with suitable cross-linking agents. As a rule, solid rubbers are vulcanized with the aid of various peroxides. Depending on the application, one can distinguish between two different kinds of peroxides. For pressure-less vulcanization of extrusion products (cables, tubes, profiles) one uses aroylperoxides which allow high reaction rates because of their low decomposition temperatures. At the same time, the rapid vulcanization inhibits bubble formation by gaseous peroxide decomposition products. A particularly favorable combination of properties – adequate storage ability at room temperature and high decomposition rate at the vulcanization temperature – is exhibited by the most-commonly used bis(2,4-dichlorobenzoyl) peroxide. Quite recently, a chlorine-free aroyl peroxide bis(4-methylbenzoyl)peroxide has also been employed.
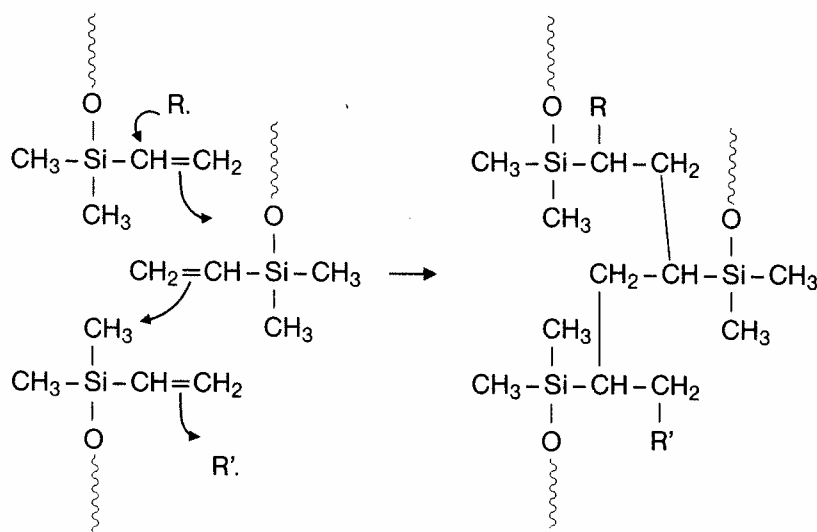
Fig. 2: Peroxidic cross-linking

The second group of peroxides, the alkyl peroxides (dicumyl peroxide, 2,5-di-tert. butyl-peroxy-2,5-dimethylhexane) decompose at the same rate only at higher temperatures. They are suitable only for vulcanization under pressure (e.g., pressed articles) but have the advantage of not forming carbonic acids as decomposition products. As a result, the relaxation properties (e.g., compression set) are not unfavorably affected. A further advantage lies in the vinyl-specific cross-linking. Above a certain "threshold concentration", alkylperoxides cause no further increase in the cross-linking density.

In contrast, aroyl peroxides cause considerable mutual bonding of methyl groups so that the hardness of the product increases steadily with increasing peroxide dose. The resultant vulcanizates exhibit a partly random distribution of the cross-links. Such elastomers exhibit markedly poorer tear strengths. Little is known at this time about the chemical structure of the cross-links.

Special investigations of model substances indicate that predominantly radical-induced addition of the vinyl groups takes place, at least for higher vinyl concentrations (see Fig. 2). This result is in agreement with alkaline-degradation experiments of vulcanizates in which a cleavage of the SiOSi- and the SiC-bonds takes place. A relatively high concentration of C_4-hydrocarbons (combination of two vinyl groups) was observed.

In contrast to the solid rubbers, liquid silicone rubbers are vulcanized almost exclusively with the aid of the platinum-catalyzed hydrosilylation reaction and therefore are formulated as two-component systems. As cross-linking agents one uses methylhydrogen-siloxanes with at least 3 SiH groups which, under catalysis by Pt(O) compounds, react with the vinyl groups of the polymers (see Fig. 3).
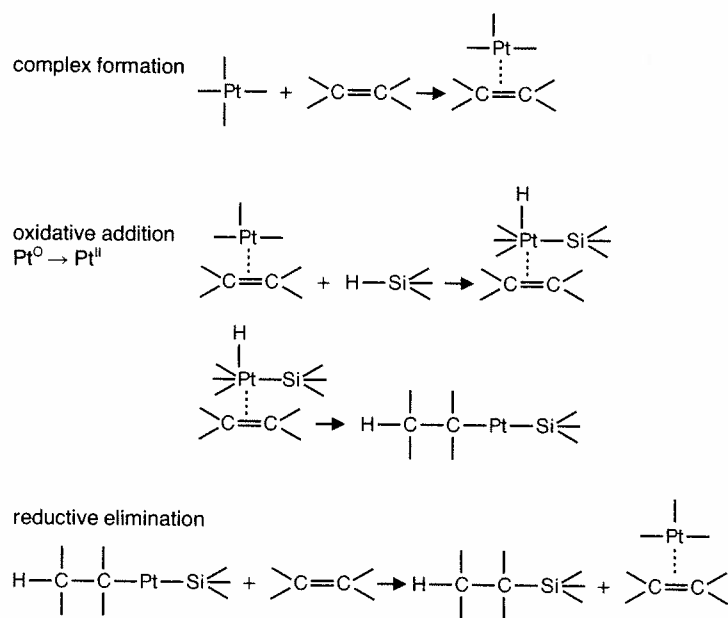
complex formation

oxidative addition
$Pt^O \rightarrow Pt^{II}$

reductive elimination

Fig. 3: Hydrosilylation (addition cross-linking)

tensile strength
MPa

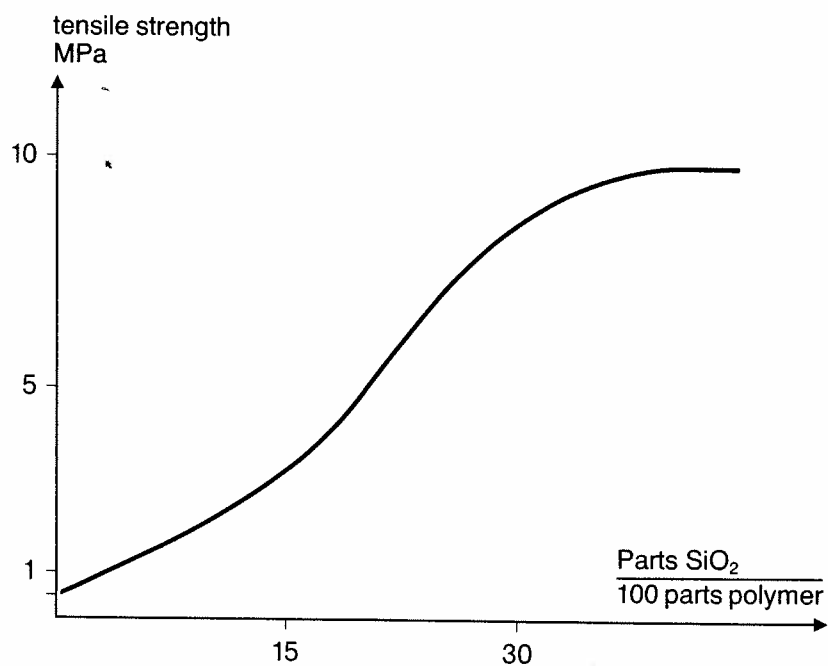$$\dfrac{\text{Parts } SiO_2}{100 \text{ parts polymer}}$$

Fig. 4: Relationship between tensile strength and amount of filler

The addition reaction is very selective. In contrast to peroxidic cross-linking, no decomposition products are formed. Stoichiometric relationship of the reactive groups can not be applied because of steric reasons. Optimal hardening, that means bonding of both vinyl endgroups of the bifunctional siloxane polymers, requires an 1.5- to 2-fold molar excess of SiH groups. The reactivity of liquid silicone rubber can be adjusted freely by varying the concentration of catalyst (usually 5–10 ppm Pt) and inhibitor.

Reinforcement by fillers

Cross-linked pure rubber polymers generally have a low tensile strengths. This does not apply to natural rubber which exhibits strongly marked crystallization during stretching. Accordingly, cross-linked polydimethylsiloxanes with their particularly low intermolecular interactions have low tensile strengths. Only with the addition of reinforcing fillers (carbon black or silica) can high-strength rubber vulcanizates be obtained. Particularly suitable are fumed silicas with BET surface areas of 150 to 400 m^2/g which increase the tensile strength about 20-fold to 10–12 MPa (Fig. 4). At the same time, viscosity is considerably increased because fumed silicas have a strong thickening effect. This effect is caused by formation of agglomerates of the primary silica particles (Fig. 5). These agglomerates build a three-dimensional network (tertiary structure) via hydrogen bonds so that the bulk density of the fumed silica is only about 50 g/l. To produce a mixture of 40 parts silica, in 100 parts polymer therefore requires addition of 8 volume parts of filler for 1 volume part of polymer. These ratios clearly indicate the necessity of using processing aids which reduce interactions between filler agglomerates as much as possible (Fig. 6). The most effective ones are hexaalkyldisilazanes which produce a completely hydrophobic silica surface. Such silylated fillers have a considerably reduced thickening effect and therefore are particularly suitable for the use in liquid silicone rubbers.
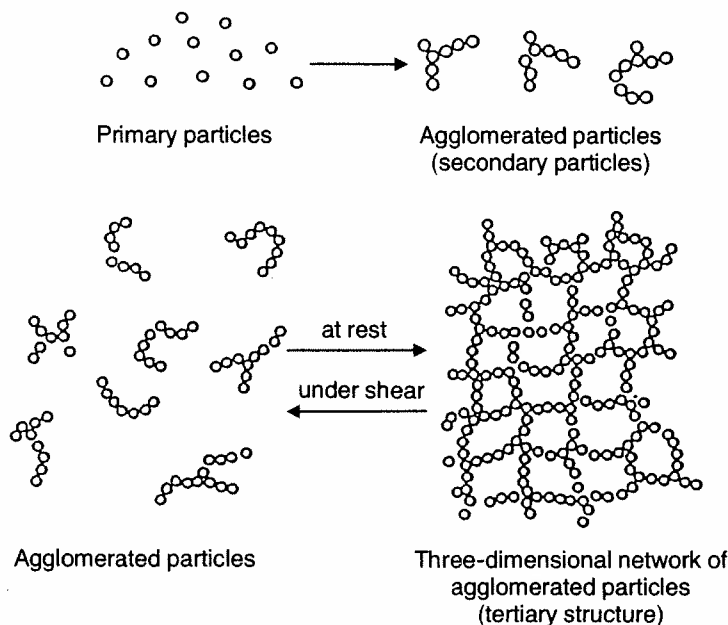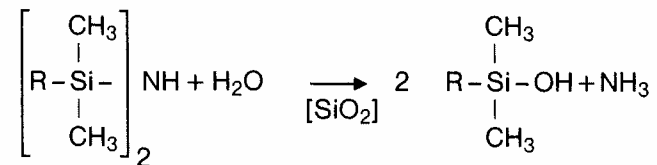

Primary particles   Agglomerated particles
(secondary particles)

Agglomerated particles   Three-dimensional network of
agglomerated particles
(tertiary structure)

Fig. 5: Interaction between silica particles

$$\left[R-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{Si}}- \right]_2 NH + H_2O \xrightarrow[{[SiO_2]}]{} 2 \quad R-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{Si}}-OH + NH_3$$

$$R = CH_3, CH = CH_2$$

$$\bigcirc Si-OH + R-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{Si}}-OH \xrightarrow[{[NH_3]}]{} \bigcirc Si-O-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{Si}}-R + H_2O$$
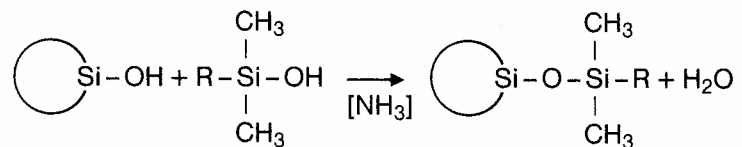
Fig. 6: Filler surface coating

before vulcanization

filler   cross-linker   polymer
A = (Si) – CH = CH₂   B = (Si) – H
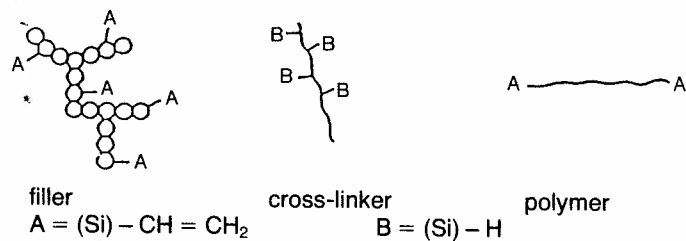
after cross-linking
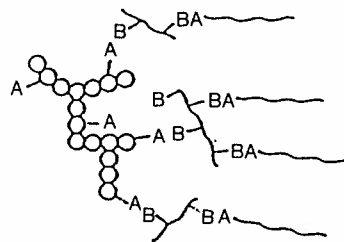
polymer-filler-network

Fig. 7: Formation of a polymer-filler-network (addition cross-linking)

In contrast, solid rubbers should have a certain rigidity. Therefore they are compounded with short-chained polysiloxanediols which have a reduced hydrophobic effect. Processing aids with vinyl groups are frequently used to achieve chemical bonding of the filler to the polymer cross-linked system and to increase the hardness of the vulcanizate. In many cases, one uses in addition to reinforcement fillers also extender fillers (ground quartz, diatomaceous earths) to increase the hardness, to reduce the degree of swelling in solvents or to achieve lower costs.

3. Properties of Rubber

Rheology

Processing of silicone rubber mixtures involves a variety of shear stresses. A comprehensive characterisation of the material therefore requires determination of the shear rate dependence of the viscosity. Because of the high concentration of filler, silicone rubbers exhibit a marked pseudo plastic behavior even at low shear rates. This applies not only to solid rubbers but also to liquid silicone rubbers (Fig. 8). For comparison, the viscosity behavior of a solid-rubber polymer is included in the figure. Below a shear rate of $D = 10^{-1}$ s^{-1}, the polymer behaves as a Newtonian liquid in contrast to liquid silicone rubbers.
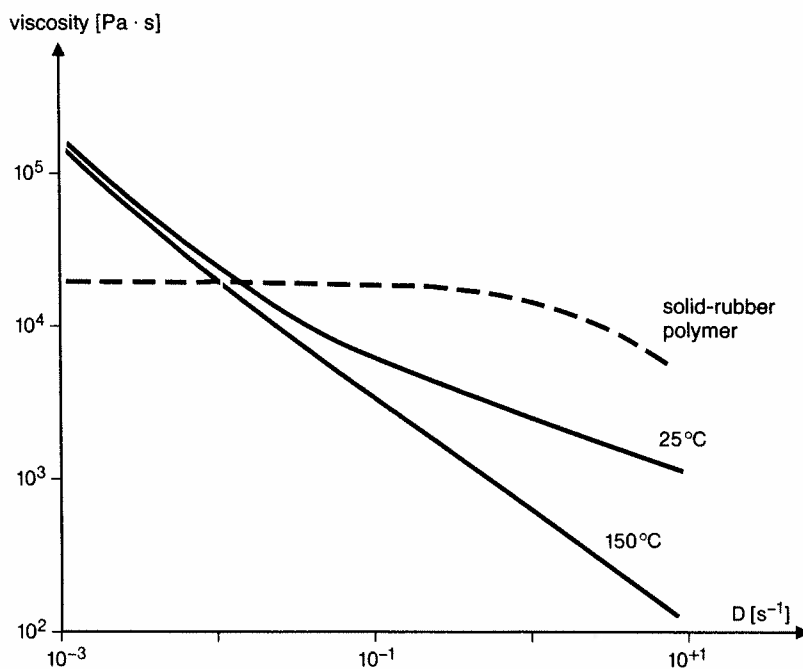

Fig. 8: Viscosity variations of liquid silicone rubbers

The small temperature dependence of the viscosity of liquid silicone rubbers at low shear rates indicates that this behaviour is controlled only by filler-filler interactions. Solid rubbers, which have much higher viscosities because of the highly viscous polymers, are even more affected by the filler-filler interactions. This becomes particularly clear if partially hydrophobic silicas are used. Such mixtures exhibit a marked viscosity increase after storage ("crepe hardening") which is reversible by replasticizing e.g., on a rubber mill. The cause lies probably in hydrogen bonds between filler agglomerates (see Fig. 5).

Cross-linking characteristics

As the name implies, hot-vulcanized silicone rubbers are vulcanized at high temperatures to keep hardening times as short as possible. In principle however it would be possible to vulcanize at lower temperatures and longer times. The curing rate depends primarily on the rates of the chemical reactions involved. Accordingly, peroxidic vulcanization of rubbers develops cross-links as fast as the added peroxides decompose into radicals. There are no notable differences between rubber types of various composition because the homolytic cleavage of the OO-bond is, in first approximation, independent of the surroundings.

In contrast, the reactivity of addition-cross-linked liquid silicone rubbers can be varied within a wide range, as already mentioned. Ordinarily, the speed of vulcanization is adjusted by Pt- and inhibitor concentrations that the pot life is at least 3 days. If one plots the time required to the development of a fixed degree of vulcanization versus temperature, one obtains a straight line in an Arrhenius plot (Fig. 9). However, the temporal
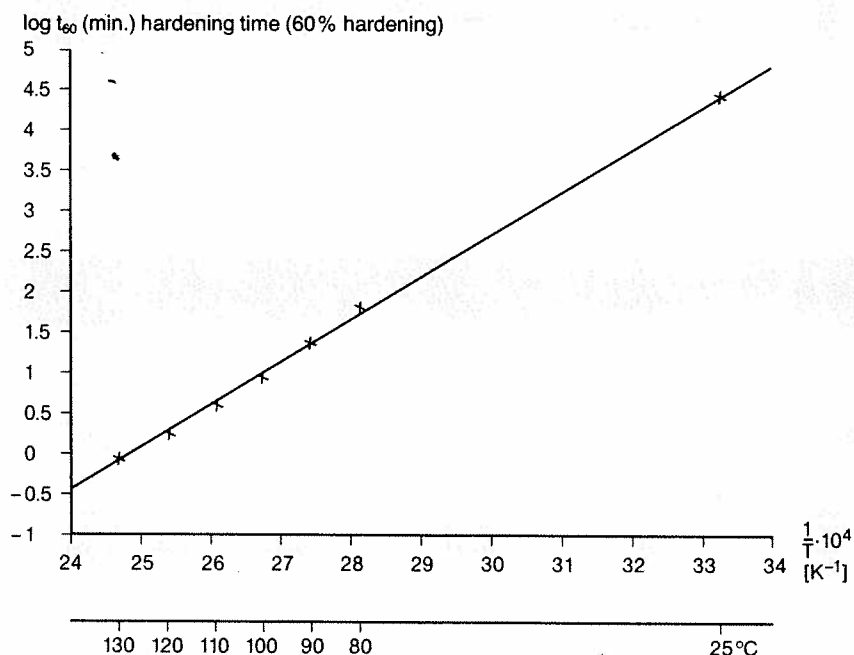

Fig. 9: Temperature dependence of the reactivity of liquid silicone rubber

progress of hardening differs markedly from ordinary chemical reactions. A similar behavior is exhibited by all rubbers. At the beginning of cross-linking, the molecules are growing with a statistical distribution of molecular weights. A three-dimensional cross-link system is then formed during the subsequent progress of the reaction.

Mechanical properties

Silicone elastomers exhibit, like other cross-linked synthetic rubbers, marked deviations from an ideal rubber-elastic behaviour. Only in the range of very small elongations (0−5%)a linear relationship between deformation and restoring force exists. However, an important condition for ideally cross-linked systems is better satisfied by silicone elastomers than by other vulcanizates. The small intermolecular interactions of the polydimethylsiloxanes impede the displacement processes during deformation and restoration less than is the case with other rubber polymers. Therefore, the rebound resilience of cross-linked silicone rubbers is, as a rule, higher and the hardness lower than for other materials. These statements apply particularly to filler-free systems. However, with increasing filler concentration, an inelastic filler structure is superposed on the elastic polymer structure, and the hardness of the vulcanizate increases. This effect is particularly strong for solid silicone rubbers with only partly hydrophobic fillers. The fillers agglomerate from their own cross-link system by hydrogen bonds. They increase the rubber viscosity as well as the hardness of the vulcanizate.

Such filler-filler interactions can be rather easily suppressed during mechanical loading. Thus, for example, the hardness decreases by up to 20 Shore units after repeated bending. The same test results in no noticeable decrease in the hardness of liquid silicone rubbers with their particularly strongly hydrophobic fillers. In comparison, they have low hardness and high rebound resilience. However, if one increases the mechanical loading (elongations over 100%), liquid silicone rubbers exhibit also a large decrease in hardness
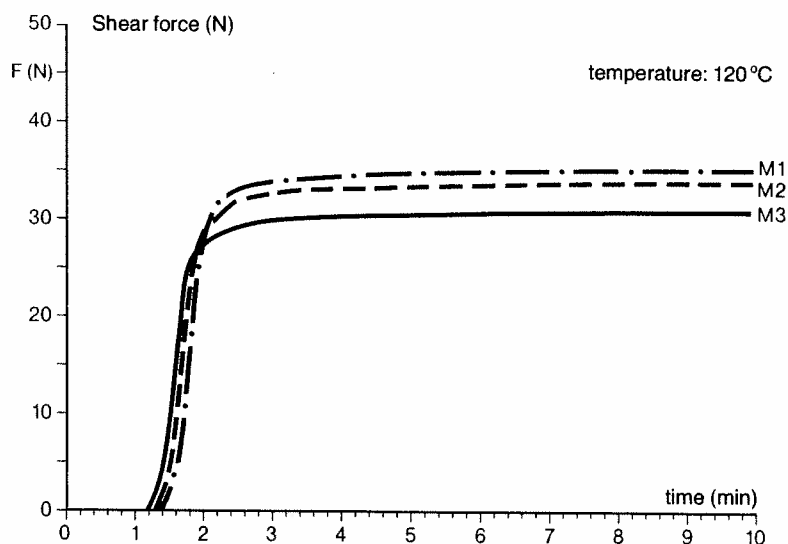

Fig. 10: Vulcanization test according to DIN 53 529 (Bayer-Frank-Vulkameter)
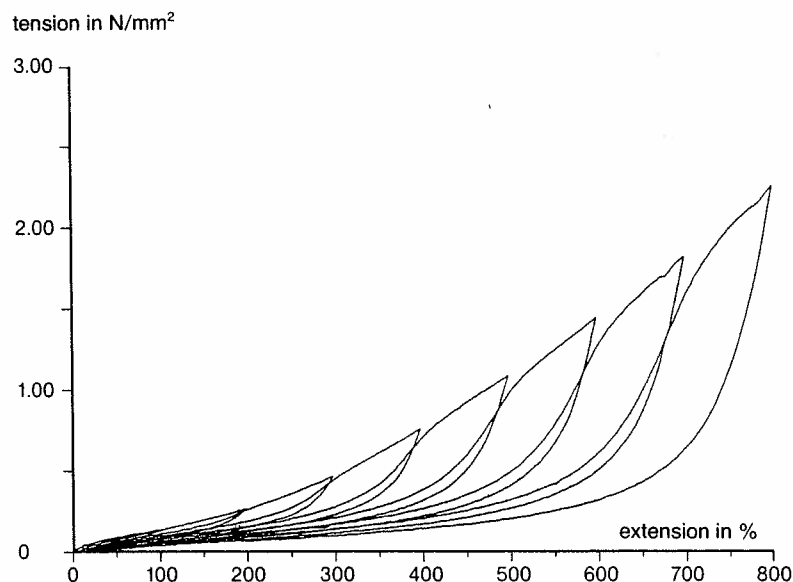
tension in N/mm²

Fig. 11: Decrease of tension with repeated extension

which shows up as a decrease of the tensile force during elongation. The same phenomenon can be observed with all filled vulcanizates. One can see in Fig. 11 how tension clearly decreases with repeated extension. In carbon black-containing synthetic rubbers, the electrical conductivity decreases at the same time because of interrupted carbon black-carbon black contacts. The original level of strength is fully maintained even after repeated loading.

Hot-air resistance

The mechanical properties of silicone elastomers show only a small dependence on temperature because of their special polymer basis. Other synthetic rubbers are much more affected by intermolecular interactions than silicone rubber and therefore exhibit higher tensile strength. However, this reinforcement effect is absent at higher temperatures (see Fig. 12).

In addition, silicone rubbers exhibit excellent hot-air resistance because their polymer chains are relatively insensitive to oxidation. This stability can be further improved by addition of stabilizers. The oxides of the elements cerium, iron, manganese, titanium and zirconium are suitable. Thus, addition of about 1 weight % red-brown iron-oxide pigment prevents a significant increase in hardness of a 50 Shore mixture at 250°C. A similar effect is obtained for platinum-catalyzed liquid silicone rubbers by addition of carbon black. In extreme cases, silicone elastomers, prepared according to special formulations, can be exposed to a temperature of 300°C for 2−3 weeks without their elongation at break becoming lower than the specified limit for elastomers of 100%.
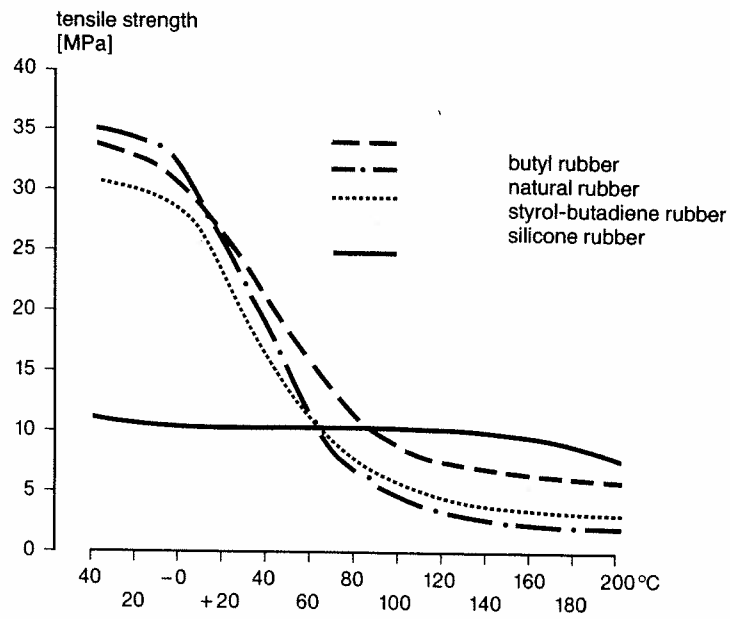
Fig. 12: Temperature dependence of the tensile strength of various elastomers
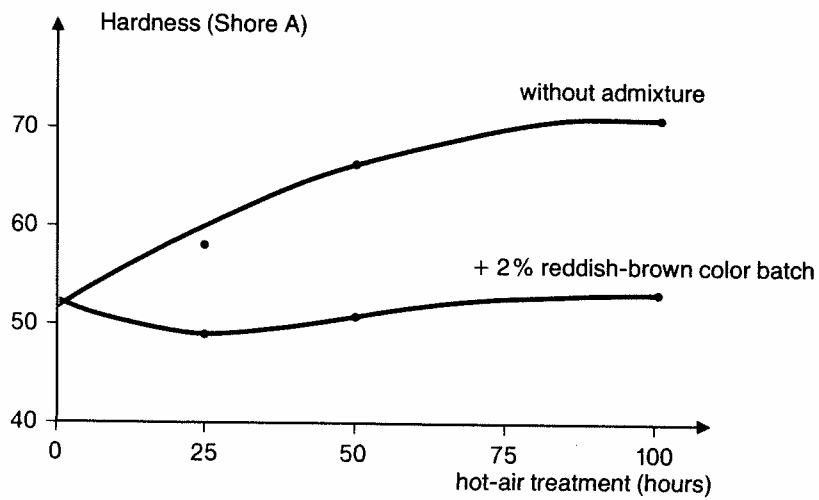
Legend:
- butyl rubber
- natural rubber
- styrol-butadiene rubber
- silicone rubber

Fig. 13: Change of hardness after hot-air treatment at 250°C

4. Processing

The processing technologies of solid and liquid silicone rubbers are different in significant aspects. Solid rubbers, because of their high viscosity (plasticized materials), are suitable for the requirements of classical rubber processing. On the other hand, liquid silicone rubbers have such a low viscosity that they can be pumped through pipelines and tubes to the vulcanization equipment. The extremely different plastic-flow behavior of these two materials is evident in the packaging of the rubbers. While solid silicone rubbers are supplied in the form of foil-wrapped bars and packed in cartons, liquid silicone rubbers are filled into hobbocks (20 l) or barrels (200 l).

Specifically, the following processing steps are required (see Fig. 14):

The solid rubber bars are removed from the packing, weighed and mixed on the two roll mixing mill with the needed amount of peroxide (plus pigment). Subsequently, a sheet of suitable thickness is taken off, cut or stamped to the required size and placed into the press mold. Processing with extrusion or automatic injection molding machines requires a rubber strip. After vulcanization, the piece is taken out of the mold, deflashed and freed of peroxide decomposition products during a period of 4−6 hours in 200°C air. The described processing technology is labor-intensive but also flexible. During calendering, which frequently includes replasticizing, other extending fillers, stabilizers, or other mixing materials can easily be worked in. Furthermore, one can produce small production series economically with cheap molds.
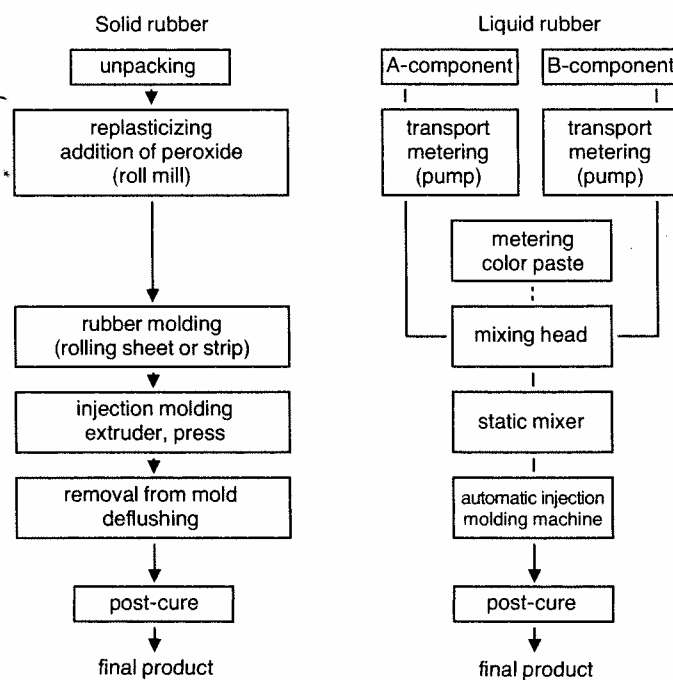
Fig. 14: Processing of silicone rubber

On the other hand, liquid silicone rubbers are more suitable for large production series of small parts. The two supplied components (A- and B-component) are transferred directly to a static mixer by a metering machine; if desired, a coloring paste is added here. In a static mixer (a pipe with mixing elements), the two components are mixed and completely automatically vulcanized and formed by an injection molding machine. If one uses cold-runner molds, even loss of material in the feed lines is avoided. Thus, liquid silicone rubbers can be processed economically without pretreatment by automatic injection molding machines in the same manner as thermoplastic materials. However in contrast to thermoplastic elastomers, which offer the same processing advantages, liquid silicone rubbers are suitable also for use at temperatures above $100°C$.

5. Outlook

Solid and liquid silicone rubbers are no longer exotic materials. Because of their special properties, they complement the application spectrum of other technical elastomers. They are being used in a steadily increasing number of applications. Only in a few cases, when above-average resistance to oils at high temperatures is needed, they are replaced by other specialty elastomers, e.g., fluoroelastomers.

The range of the present-day spectrum of applications becomes clear from the following list of typical silicone-elastomer parts:

1. Extrusion parts (solid rubber)

- transparent tubes for the food industry and for medical technology
- cable insulation for applications at high temperature (e.g., flat irons)
- sealing materials (seals for oven doors)

2. Pressed articles (solid and liquid silicone rubber)

- key boards
- plug boots
- anode caps (television)
- ppc rolls
- baby nipples and pacifiers
- technical small parts (cable connectors, O-rings)

Hot-vulcanized silicon rubbers will continue to contribute disproportionately also to the future growth of technical elastomers.

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