5.1. Introduction

Nomenclature and Structure. Because silicones (also called siloxanes) have an inorganic backbone, they should be represented pedantically as inorganic polymers and named according to IUPAC rules for inorganic polymers. However, because many silicones depicted in this section also contain organic subunits, all silicone CRUs in this section are oriented according to IUPAC **organic** rules, which state that O is senior to Si. See → Polymer Nomenclature for more information about orienting CRUs correctly.

The term silicones is used for compounds in which silicon atoms are linked via oxygen atoms, each silicon atom bearing one or several organic groups. In industrially important silicones, these groups are usually methyl or phenyl. The silicones are known as polyorganosiloxanes according to IUPAC rules.

The structure of the industrially important "methylsilicones" can involve the units listed in Table 1.

Polymer structures can be described by using the letters M, D, T, and Q to designate the monomer units. Linear silicone fluids are composed mainly of D units. The base polymers for silicone elastomers or silicone rubbers consist of D units that bear cross-linkable functional groups. The main structural feature of the highly branched silicone resins are T units, often combined with D units to make the resins more flexible. Silicone resins can also contain Q and M units.

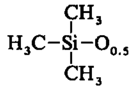
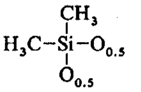
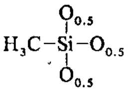
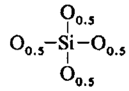
General Properties. Silicones have many outstanding properties, which are described in detail for the individual product groups. In general, methylsilicones exhibit greater stability to high temperature, UV radiation, and weathering than organic polymers; marked surface-active behavior (low surface tension, high spreading power); good dielectric properties, as well as low temperature dependence of their physical properties.

5.2. Linear and Cyclic Polyorganosiloxanes

5.2.1. Production

Linear and cyclic polyorganosiloxanes are generally produced by reacting organodichlorosilanes with water. The mixture of oligomeric siloxanes arising from hydrolysis can be converted either entirely to cyclic siloxanes (e.g., octamethylcyclotetrasiloxane) or directly polymerized to linear polysiloxanes. A special case of the production of cyclic or linear oligomeric dimethylsiloxanes that has gained in importance is the methanolysis of dimethyldichlorosilane.

Table 1. Origin, functionality, and fields of application of silicone structural units

Starting compound	Structural unit		Application
	Symbol	Functionality	
$(CH_3)_3SiCl$ Monochloro-trimethylsilane	M	 $H_3C-\overset{CH_3}{\underset{CH_3}{Si}}-O_{0.5}$ monofunctional	chain end in silicone fluids, trimethylsilyl protecting groups
$(CH_3)_2SiCl_2$ Dichlorodi-methylsilane	D	 $H_3C-\overset{CH_3}{\underset{O_{0.5}}{Si}}-O_{0.5}$ difunctional	linear siloxane polymers, silicone fluids, rubbers, elastomers
CH_3SiCl_3 Trichloro-methylsilane	T	 $H_3C-\overset{O_{0.5}}{\underset{O_{0.5}}{Si}}-O_{0.5}$ trifunctional	silicone resins for paints, impregnating agents, masonry protection
$SiCl_4$ Tetrachloro-silane	Q	 $O_{0.5}-\overset{O_{0.5}}{\underset{O_{0.5}}{Si}}-O_{0.5}$ tetrafunctional	silicone resins

The most important chlorosilanes used industrially (> 90 % of the total) are the methylchlorosilanes. Other chlorosilanes that contain silicon-bound H, C_6H_5, $CH_2{=}CH$, or CF_3CH_2-CH_2 groups, either exclusively or in combination with methyl groups, are produced in smaller quantities. Chlorosilanes and siloxanes containing other organic ligands, such as C_2H_5 or $HOCH_2$, are not discussed in detail here because of their minor importance.

5.3. Silicone Fluids

The structure of linear silicone fluids can generally be described by the composition MD_xM ($x = 2-4000$).

Silicone fluids are distinguished from common organic fluids by a number of unique properties:

1) Good thermal stability (150 – 250 °C)
2) Good low-temperature performance (<-70 °C)
3) Strong hydrophobicity
4) Excellent release properties
5) Antifriction and lubricating properties
6) Pronounced surface activity
7) Good dielectric properties
8) Very good damping behavior
9) Good radiation resistance
10) High solubility of gases
11) Physiological inertness
12) Low temperature dependence of physical properties

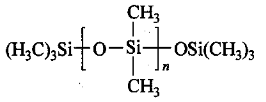
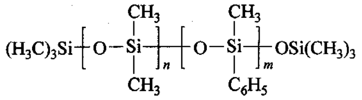
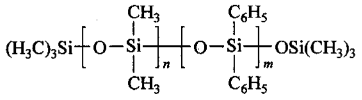
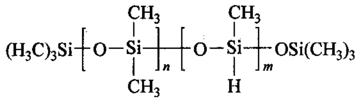
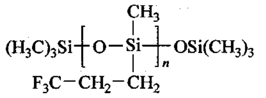
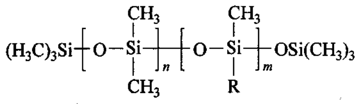
These properties can be modified over a wide range by varying the organic substituents. The most important silicone fluids are listed in Table 4.

5.3.1. Methylsilicone Fluids

The most important silicone fluids are the methylsilicone fluids (polydimethylsiloxanes, PDMS). Silicone fluids exhibit a chain-length distribution. The average chain length largely determines the viscosity. Low molecular mass volatile constituents are removed during production, which increases the flash point of the final product. Fluids with viscosities ranging between 1 and 10^6 mPa · s are commercially available.

The most important physical properties of polydimethylsiloxanes are listed in Table 5, which shows that the physical properties of silicone fluids depend on the molecular mass only up to a certain degree of polymerization. With increasing molecular mass, they reach a limiting value.

Table 4. Important types of silicone fluid

Structural formula	Brief designation
 $(H_3C)_3Si-\left[O-\overset{CH_3}{\underset{CH_3}{Si}}\right]_n-OSi(CH_3)_3$	methylsilicone fluids $n = 2-4000$
 $(H_3C)_3Si-\left[O-\overset{CH_3}{\underset{CH_3}{Si}}\right]_n-\left[O-\overset{CH_3}{\underset{C_6H_5}{Si}}\right]_m-OSi(CH_3)_3$	methylphenylsilicone fluids $n = 0-1000$, $m = 1-1000$
 $(H_3C)_3Si-\left[O-\overset{CH_3}{\underset{CH_3}{Si}}\right]_n-\left[O-\overset{C_6H_5}{\underset{C_6H_5}{Si}}\right]_m-OSi(CH_3)_3$	methylphenylsilicone fluids $n = 0-1000$, $m = 1-1000$
 $(H_3C)_3Si-\left[O-\overset{CH_3}{\underset{CH_3}{Si}}\right]_n-\left[O-\overset{CH_3}{\underset{H}{Si}}\right]_m-OSi(CH_3)_3$	methylhydrogensilicone fluids $n = 0-100$, $m = 1-100$
 $(H_3C)_3Si-\left[O-\overset{CH_3}{\underset{F_3C-CH_2-CH_2}{Si}}\right]_n-OSi(CH_3)_3$	fluorosilicone fluids $n = 10-100$
 $(H_3C)_3Si-\left[O-\overset{CH_3}{\underset{CH_3}{Si}}\right]_n-\left[O-\overset{CH_3}{\underset{R}{Si}}\right]_m-OSi(CH_3)_3$	methylalkylsilicone fluids $n = 0-100$, $m = 1-100$

5.3.6. Applications

The characteristic properties of silicone fluids are exploited in numerous applications [22]. Thus, because of their high thermal stability and good low-temperature performance, they are used as *heat-transfer media* in heating circuits in the chemical, petrochemical, pharmaceutical, and food industries and in solar power plants, and as *refrigerants* in cryostats, freeze dryers, and climate simulation plants. Their low surface tension leads to use as *release agents* in the processing of plastics and rubber articles. Silicone fluids, especially functional copolymers with Si – H or Si – OH groups, spread on surfaces to form oriented films with their hydrophobic organic groups aligned opposite to the phase boundary of the substrate. These functional copolymer fluids have many uses as additives in water-repellent *polishes*, as *waterproofing agents* for textiles, and as *protective coatings* for building materials. Their high water vapor permeability is a particular advantage, permitting good ventilation of water vapor while largely preventing the entry of liquid water.

Because of their surface activity, polydimethylsiloxanes are used as *antifoams* in aqueous systems, in petroleum processing, and in laundry detergents. Special formulations with highly dispersed silica are effective antifoams even in the part-per-million range. In human and veterinary medicine, siloxane antifoams are used as *antiflatulent* agents. The antifriction properties of polydimethylsiloxanes make them useful as *lubricants* (e.g., for films, yarn, medical articles, wine corks, and fillers). Special silicone fluids that dissolve spermicides of the Nonoxinol-9 type can be used as prophylactic coatings for condoms. Silicone fluids are increasingly important as *dielectric coolants* for transformers and rectifiers because of their flame resistance [23], resistance to ageing, material compatibility, and physiological inertness. These properties are also important for use as *power transmission fluids* in viscous and fan couplings [24] and as *hydraulic* and *damping fluids* in shock absorbers, railway buffers, and vibration insulation systems, at both high and low temperature. The more advantageous lubricating properties of siloxanes compared to pure organic products in the temperature range from less than – 20 °C to > 150 °C have led to their use as *lubricants*. The greases or pastes obtained by incorporating consistency improvers exhibit a particularly good lubricating behavior when the base fluids are modified by phenyl, long-chain alkyl, or fluoro groups. They are used chiefly for lubricating electric motors, motor bearings of furnace blowers and ventilators, pump bearings for liquid gases, and machine bearings for low-temperature operation. Flexure-stable silicone fluid pastes are used as *embedding compounds* for glass-fiber cables in communication engineering. Since silicone fluids have a good dissolving power for organic vapors, they can be used as *absorbents* for organic vapors of low water solubility in off-gas purification. Modified silicone fluids are used as *paint* *additives* to influence the leveling or to obtain special finishes (e.g., hammer effect). Their tolerance by the skin and their physiological inertness [25] make silicone fluids suitable as additives for *ointments* and *cosmetic preparations.*

5.4. Silicone Rubbers and Elastomers

5.4.1. General Properties

Silicone polymers exhibit low glass transition and equilibrium melting temperatures, weak intermolecular interactions, and high chain mobility. These properties make them highly suitable for use in rubbers.

Silicone polymers can incorporate a variety of functional groups as potential cross-linking points. The position (exclusively chain ends, or along the polymer chain) and the content of these functional units can be readily varied. Together with the wide range of polymers and their compound viscosities these different cross-linking systems lead to many applications.

The development of silicone elastomers is reviewed in [26] – [28]. Specialized rubbers with unique properties such as low-temperature flexibility down to –70 °C according to DIN 53548 (phenyl, ethyl) [29], oleophobicity and solvent resistance (fluoroalkyl, cyanoalkyl), or higher surface tension (polyether) are obtained by replacing the methyl groups with other organic groups.

Curing (vulcanization) converts unvulcanized silicone compounds into silicone rubbers/elastomers. Unlike other rubber polymers, unfilled silicone rubbers achieve only low mechanical strengths when cured. Adequate strengths are only obtained by incorporating reinforcing fillers. High surface area silicas are used almost exclusively for this purpose.

The stress – strain curves of filler-free siloxane networks at small deformations can be well described by the semi-empirical Mooney – Rivlin equation [30], [31]. The ultimate strength of silicon elastomers is determined by the attainable average chain length between cross-links [32]. The Einstein – Guth – Gold equation is also used to describe filled silicone elastomers [33].

5.4.8. Paper and Textile Coatings

Silicone elastomers are used in a variety of coating applications. The most important substrates are paper and textiles. The choice of polymer and curing system, the formulation and the coating method depend on the substrate and the desired properties.

5.4.8.1. Paper Coating

Paper and films are often coated with very thin layers of silicone to make them repellent to adhesive substances.

Paper coating plants operate at high speed (up to 500 m/min), and thus require silicone coating systems that cure rapidly while maintaining a sufficient pot life. Silicone coating materials are two- or multicomponent systems that cure at substrate temperatures of 100 – 130 °C in 5 – 15 s.

The coating mixture must exhibit good wetability, both for the rolls and for the substrate surface, to give pore-free films. Completely cured coatings contain no migrating constituents that can impair the adhesive properties of a subsequently applied adhesive layer. The adhesive is applied directly (on-line process) or in a later manufacturing step. The adhesive forces between the adhesive layer and the silicone coating must remain constant over fairly long periods of storage. This is especially important when controlled-release additives are used to increase adhesion between the silicone and adhesive layers.

At present, the following silicone coating systems are used:

Solvent-Containing Systems. *Condensation systems (I)* consist of hydroxyl-end-capped polydimethylsiloxanes and polymethylhydrogensiloxanes as cross-linkers. The cross-linking reaction is catalyzed by organotin compounds:

$$\equiv SiOH + HSi\equiv \xrightarrow{Sn} \equiv SiOSi\equiv + H_2$$

The system is used in dilute form (3 – 5 % in organic solvents). In emulsion form it is diluted to about 10 % with water before use.

Condensation systems (II) contain reactive silanes instead of polymethylhydrogensiloxane. Their curing mechanism is the same as for the moisture-cured RTV compounds (see Section 5.4.4.3). Systems I and II have been virtually displaced from the market by hydrosilylation-cured systems because of disadvantages such as sensitivity to variations in atmospheric humidity and slow cure even at high curing temperature (20 – 40 s at 120 – 180 °C).

Hydrosilylation-cured systems consist of higher viscosity polydimethylsiloxanes with reactive vinyl groups and polymethylhydrogensiloxanes as cross-linkers. They cure in the presence of platinum complexes (30 – 120 ppm Pt) in 15 – 20 s at 120 – 140 °C (for curing mechanism see Section 5.4.4.2). They are applied as solutions in organic solvents or as emulsions. With sufficient dilution it is possible to prepare very thin films. The solvent is removed by evaporation during cross-linking and is recovered or burned.

Solvent-Free Systems. *Heat-cured systems* are also based on the principle of hydrosilylation curing and differ from the corresponding solvent-containing systems by having shorter-chain vinyl-containing polymethylsiloxanes with a viscosity of 200 – 500 mPa · s. In contrast to solvent-containing systems, the thickness of the solvent-free coating does not change on curing. Therefore, stringent requirements must be met by both the application equipment and the substrates to obtain pore-free films with reproducible coating thicknesses of ca. 1 μm (ca. 1 g/m^2) silicone. Solvent-free systems cure in 5 – 15 s at substrate temperatures of 100 – 120 °C. About 50 % of all substrates are coated with solvent-free systems, and the proportion is increasing.

Photochemically cured systems are not well established in paper coating, in spite of the advantage provided by minimal thermal treatment of the substrates. This method is, however, used for special coating applications [98]. The cross-linking mechanisms are varied, but most systems use UV-absorbing sensitizers to increase the quantum yield.

Radiation-cured systems use high-energy radiation (e.g., electron beams) and do not require sensitizers, but they do require a nitrogen atmosphere to avoid formation of interfering oxygen radicals.

Silicone-coated papers and films are assessed by the following criteria:

Curing of the coating
Abrasion resistance (no rub-off)
Adhesion to the substrate
Porosity of the coating
Magnitude of the release force values
Constancy of the release force values
Residual adhesive forces
Coating strength
Film smoothness

Fields of application for the abhesive coated papers are [100]

Self-adhesive labels (74 %)
Adhesive tapes (10 %)
Hygienic articles (6 %)
Construction, packaging, decoration, etc. (10 %)

5.4.8.2. Textile Coating

Textiles can be rendered water-repellent with special silicone fluids that simultaneously provide the fabric with a soft feel. Elastomer systems that are similar in composition to those described for paper coating or for two-component and LSR silicone rubbers are used for waterproof textile coatings that are permeable to water vapor.

5.4.9. Properties of Silicone Elastomers

The typical properties of silicone polymers are also exhibited by cured silica-reinforced products. They account for the many applications of silicone elastomers. Different combinations of properties can be obtained by choice of polymer, cross-linking system, and compound composition.

Temperature Limits for Silicone Elastomers. Silicone elastomers have the widest operating temperature range of commercially important rubbers. VMQ rubbers exhibit better relaxation properties than other synthetic rubbers, i.e., the compression set has a smaller temperature dependence in the range –40 to 170 °C (Fig. 10) [99].

Mechanical properties such as tensile strength and tear strength also show only a small temperature dependence between – 40 and 150 °C. The tensile strength of VMQ is strongly enhanced at – 40 °C.

This general behavior must be distinguished from heat stability or changes in the room temperature properties that occur at elevated temperature. The heat stability of elastomers is evaluated by measuring the retained properties after high-temperature ageing (see hot-air resistance).

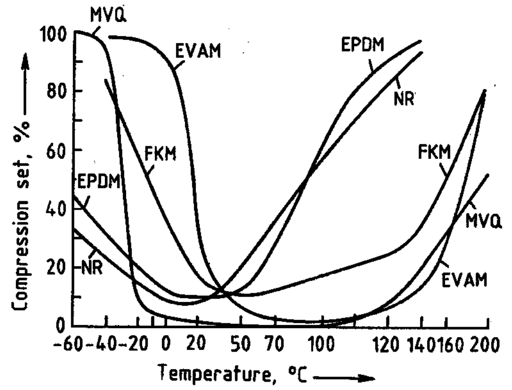


Figure 10. Compression set versus temperature for some elastomers

A phenyl content of 5 – 12 mol% extends the low-temperature flexibility (measured as torsional stiffness, DIN 53 548) from – 45 to – 70 °C and the brittleness point from – 55 to – 105 °C (ASTM D 380) [88].

Phenyl groups improve the resistance to γ rays by a factor of 2 – 5.

Hot-Air and Oxidation Resistance. The high-temperature and oxidation resistance of pure cross-linked polydimethylsiloxane polymers is adequate only up to 200 °C. Above this temperature, oxidation reactions at the alkylene cross-links and methyl groups cause embrittlement. Oxidation can be inhibited by using hot-air stabilizers (see Section 5.4.2). Further improvement is achieved by limiting the content of acidic Si – OH groups in the silica filler.

Since even low contents of acidic and alkaline impurities lead to depolymerization (reversion) of the network, the polymers must be thoroughly neutralized. Stabilizers that neutralize acidic decomposition products from cross-linking agents, for example, are added optionally. Elastomers stabilized in this way withstand exposure to hot air at 300 °C for up to 21 d. After an induction period, embrittlement increases logarithmically with time.

Steam, Chemicals and Oil. Despite the sensitivity of the Si – O bond to acids, bases, and to water at elevated temperature, the stability of silicone elastomers can be significantly improved by increasing the cross-linking density and by using additives [52], [101].

Patents describe the use of combinations of CaO and silanes containing methacrylic groups to improve the oil resistance [102]. Additives such as mica or diatomaceous earth have a similar effect [103], [104]. The swelling rate can be appreciably reduced by using fairly large amounts of vinyl resins [105]. Stabilized VMQ rubbers withstand immersion in ASTM 2 oil for up to 2000 h and in ASTM 3 oil for up to 500 h.

Swelling rate depends on the solubility parameters χ of the siloxane and the contact medium. Similar χ values result in higher swelling rate [106]. Additional degradation by acids or bases occurs in technical applications. Silicone elastomers with enhanced oil resistance usually have a high filler content and thus a reduced siloxane and stabilizer content.

A large decrease in the swelling rate can be achieved by changing the solubility parameter of the polymer (e.g., by using fluoroalkyl-modified siloxanes) [89].

Another method to improve the oil resistance is to blend silicone elastomers with solvent-resistant rubbers such as acrylonitrile or fluorinated rubbers [107] – [110]. These blends can exhibit improved low-temperature and swelling behavior. Interest in blends has increased with the introduction of new peroxide-curable fluorinated rubbers [107], [111].

Reversion – Compression Set. Reversion and increased compression set are often induced by the action of water vapor and acid or base. The resulting breakdown of the polymer network can be counteracted by polymer neutralization and by using the maximum possible cross-link density. Compression set can also be reduced by using neutralizing additives or by the addition of methylhydrogensiloxanes [52], [101], [112].

High-Strength Formulations. The room-temperature tensile strength of silicone elastomers of 6 – 12 MPa is lower than that of other common elastomers (10 – 30 MPa). The tear strength is also only moderate (10 – 30 N/mm, compared to 20 – 80 N/mm), according to ASTM 624 D die B. Much effort has been targeted at improving the tear strength of silicone elastomers [113] – [119]. The tear propagation strength can be increased to 40 – 55 N/mm by optimizing the polymer structure.

Adhesion. Silicone elastomers are often used in composite structures with other materials. Here, adhesion of the elastomer to the other material is particularly important.

Owing to their cross-linking mechanism, condensation cross-linking systems show good adhesion to surfaces with hydroxyl groups. The hydroxyl groups on the surface react with the SiOH or SiOR groups of the polymer. Good adhesion is observed to glass and to metals with oxide or hydrated surfaces, such as aluminum and iron. Condensation systems with and without solvent are also used as coupling agents or adhesives for other silicone elastomers.

For good adhesion peroxide- and hydrosilylation-cured rubbers frequently require primers that are applied as coupling agents to the surface of the material. With the proper choice of primer, good adhesion can even be obtained on many plastic surfaces [120] – [123].

Electrical Properties. Siloxanes and their mixtures with pyrogenic silica have a very good electrical insulating capacity. The electrical properties are temperature dependent and are strongly affected by exposure to water. Accordingly, the resistivity of $10^{16}\ \Omega \cdot \mathrm{cm}$ under dry conditions at 20 °C decreases to $10^{12}\ \Omega \cdot \mathrm{cm}$ at 160 °C and 50 % R.H. [32].

The use of precipitated instead of pyrogenic silica leads to a decrease in resistivity and, because of the higher water content of the filler, to an increase in dielectric constant. The addition of carbon blacks [124], sometimes in combination with conducting powders or fibers [125], [126], can lower the resistivity to 3 Ω · cm (ISO 1853).

Thermal Properties. The thermal conductivity of silicone elastomers can be increased by large amounts of inert fillers such as quartz, AlN, Al_2O_3, Si_3N_4, or MgO [41], [43], [127], [128].

Burning Properties. The heat evolution from siloxanes on burning is lower and accordingly more favorable than that of pure organic elastomers [129], [130]. A residual electrical insulating capacity is maintained, even after burning, as a result of the remaining silica framework.

Flame retardants can effectively suppress the further combustion of silicones after ignition. In this way, transparent or colored elastomers can be produced that pass flammability tests such as UL 94 V1 or V0 [59]. The combustion gases formed are less toxic than those from halogen- or nitrogen-containing elastomers [129] – [132].

Gas Permeability. Silicone elastomers dissolve many gases well and are highly permeable. The high gas permeability [133] is somewhat selective and depends on the substituents [134] – [137]. Silicone elastomers are therefore suitable for the production of gas-separation membranes [138] and for oxygen-permeable contact lenses or dressings for wounds [139] – [141].

Transparency. The extremely small primary particles of well-dispersed high surface area silica fillers in silicone elastomers cause only minor light scattering. With a UV transmission (DIN 5033) of up to 90 %, they are almost transparent [46] and are therefore used as contact and other lenses [140]. This high transparency is achieved by special hydrophobic treatment of the filler with strong silylating agents [142]. A further enhancement of the transparency is possible by incorporating phenyl groups into the polymer, which shifts the refractive index n_D^{20} from 1.39 to 1.43 – 1.47 [143] – [145]. Recently, more rigid silicone – acrylate copolymers have been preferred for contact lenses [146].

Physiological Behavior. Because silicone elastomers exhibit low surface tension and are abhesive, interactions with surfaces of living tissues, cells, or blood platelets are very weak [146] – [148]. Therefore, filler-free elastomers, in particular, are suitable for implant applications. Numerous surgical and medical applications exist. Another advantage of silicone elastomers is that they can be sterilized in steam above 100 °C.

5.4.10. Applications

The typical properties of silicone elastomers lead to their application in areas involving:

1) Electrical insulation or conduction
2) High and/or low temperatures
3) Weather and UV exposure
4) Oil and hot-air contact
5) Dynamic stress
6) Flame resistance, arcing resistance
7) Gas permeability
8) Contact with foods
9) Contact with living tissue
10) Abhesive surfaces
11) Transparent articles of high optical quality

Examples of uses of silicone elastomers are listed below:

Electrical
- wire insulation
- cable sheaths
- power cable endcaps

Electronic
- anode caps
- coatings
- encapsulation
- fiber-optic coatings

Household
- pot seals
- coffeemaker tubes and seals
- baby bottle nipples
- oven gaskets
- anti-stick papers

Automobile
- gaskets
- cable guides and connectors
- headlight seals
- shaft seals
- O-rings
- cooling and turbo hoses
- oil pan gaskets
- spark plug boots

- air bags
- ignition cables
- fuel line diaphragmas and seals
- exhaust pipe hangers
- axle boots

Airplane

- headlight seals
- window seals
- interior joints and floors
- vibrational damping

Office machines

- keyboard pads
- copier rolls

Medicine and dentistry

- tooth impression compounds
- implants
- pumps
- heart valve seals
- catheters
- membranes
- lenses
- controlled drug release

Paper and Textiles

- coatings
- conveyor belts

General

- casting forms
- membranes
- impression molding compounds
- anti-stick bladders
- divers' masks
- protective masks