The Chemistry and Properties of the Medical-Grade Silicones

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Medical-Grade Silicones

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SUMMARY

The medical grade silicones are probably the most widely used of all
the synthetic polymers for permanently implanted subdermal devices.
This paper reviews the chemistry of these materials from the original
polymer manufacturing through the various stages necessary to obtain the
types of heat vulcanizing silicone rubber, room temperature vulcanizing
silicone rubber, and silicone rubber adhesive most commonly used in
medical applications.

INTRODUCTION

The family of silicones, since it became commercially available in 1943,
has grown to be a group with many and varied members. This growth has
resulted from the fact that they can fulfill many of the specialized demands
of modern technology.

The medical applications of these materials have developed in much the
same manner: In its constant search for better methods of combating
human frailty the medical fraternity uncovered the unexpected property of
physiological inertness in certain silicones and, with the help of industry,
has now applied them in many ways.

The first medically oriented use of these new materials was predicated
on the theory that if a material could make glass nonwetting, it would

delay the clotting of blood in contact with the glass. Since even the sili-
cones of the 1940's were very effective in treating the surface of glass, they
were tried and found to increase the clotting time substantially. They still
are used to siliconize blood-contacting surfaces. There are few materials
that are more effective, and these are available only by dint of great effort.

The mental step of extrapolating the delaying of blood clotting to non-
reactivity against tissue, while perhaps not entirely a logical one, was at
least an easy one, and it was made early. Tentative attempts at the sub-
dermal use of silicone rubber were made in the late 40's. In 1953, in
answer to requests from research physicians, Silastic S-9711, the first
silicone rubber made specifically for such investigations, was developed.
(Silastic is a registered trade mark of Dow Corning Corp.)

With the establishment of the Dow Corning Center for Aid to Medical
Research in 1959, an improved version of this and other types of silicone
rubber designed for medical use were developed to answer the wide variety
of requests. In 1962 the Dow Corning Medical Products Division was
established. The medical use of the silicones had come of age.

Great strides in the technology of the silicones themselves and in their
medical applications have been made in the past 10 years with the result
that they are now the most widely used implantable synthetics.

This paper will concern itself with the general chemistry of those
silicones most widely used in medicine, and it is designed to be under-
stood by the physician whose chemistry courses were taken some years
ago. The medical-grade silicones are based upon the same chemistry in-
volved in making all silicones, and those who wish finer detail can
consult any one of the excellent texts on the subject [1-4].

Voluminous data on the medical applications of the silicones are avail-
able elsewhere and will not be discussed in detail here.

The ability to make silicones is based on the fact that the carbon in
many organic compounds can be replaced with silicon, thus combining the
families of organic and inorganic chemicals. By the proper tailoring of the
molecules, it is therefore possible to combine some of the inertness in-
herent in quartz with the tractability and softness of rubber and oil.

While silicones can be, and are, made with many different organic
radicals, the dimethyl type is most common and will be used here to
illustrate the following very simplified procedure for their manufacture.

SILICONE POLYMERS

The first step in the production of a silicone is the reduction of silica
to elemental silicon:

$$SiO_2 + C \rightarrow Si + CO_2$$
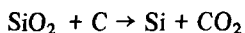
The silicon is then reacted with methyl chloride. Under the proper conditions this results in dimethyl dichlorsilane:

$$Si + 2CH_3Cl \rightarrow \underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{Cl-Si-Cl}}$$

When the dimethyl dichlorsilane is contacted with water, a polymer is formed. This probably proceeds through the following steps:

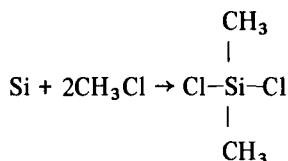$$\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{Cl-Si-Cl}} + 2HOH \rightarrow \underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{OH-Si-OH}} + 2HCl$$
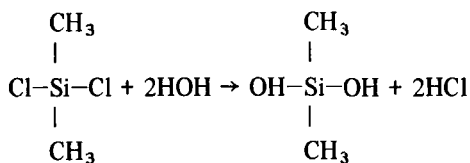
The diol is extremely unstable and immediately condenses with a neighbor to form water and a silicone polymer:

$$\underline{OH} \underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{-Si-O}}\boxed{H + OH}\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{-Si-O}}\boxed{H} \rightarrow HOH + \underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{-Si-O}}\left[\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{-Si-O}}\right]_x\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{-Si-O-}}$$
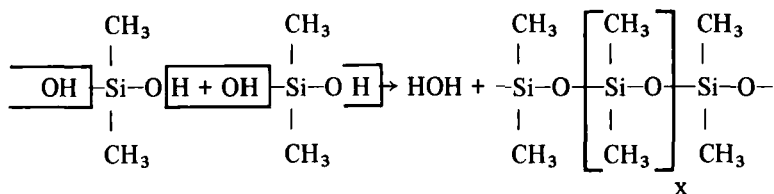
The polymer chains are probably terminated by OH groups. If hexamethyl disiloxane

$$\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{CH_3-Si}}-O-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{Si-CH_3}}$$
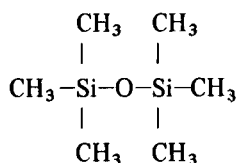
is added and the mixture equilibrated, polymers endblocked by

$$CH_3$$
$$|$$
$$-Si-CH_3$$
$$|$$
$$CH_3$$
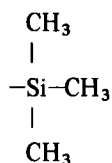
and with predetermined average molecular weights can be obtained. These polymers are clear, water-white fluids with their viscosity determined by the average length of the polymer chain. Table 1 shows the relationship of the

Table 1. Viscosity of Polydimethyl Siloxane Compared to
Average Length of the Polymer Chain

Viscosity (cSt)	Approximate number of dimethyl siloxy units	
	By number average molecular weight	By weight average molecular weight
.65	2	2
1.00	3	3
2	5	5
10	16	17
50	46	60
100	70	100
350	130	200
1,000	200	350
10,000,000	3,000	5,400

viscosity of dimethyl siloxane polymers, as measured in centistokes, to the approximate number of dimethyl siloxy units, as determined by two methods, the weight-average molecular weight and the number-average molecular weight. It is felt that of these two equally valid procedures, the weight-average molecular weight method is preferred.

SILICONE RUBBER

Silicone rubber is made from these silicone polymers, just as organic rubber is made from butyl polymer or from the natural polymers of the hevea tree.

Most rubbers are compounded with polymers, fillers, additives, and vulcanizing agents. The fillers give additional strength to the polymer; the additives are used for a wide variety of purposes, such as color, plasticizing, antioxidation, and heat stability; and the vulcanizing agents serve to change the raw mass from a plastic to a true rubber.

The vulcanization of a polymer is simply the tying together of the hitherto separate polymer chains. When the polymer chains are not tied together, as is the case in a fluid polymer, they can move around in respect to one another. If the chains are short ones, the movement is easy, and thus the polymer has a low viscosity. If the chains are long ones, they are snarled together and are more difficult to separate, so the viscosity is higher. If they are tied together at a few points, they become a network that can be separated only by rupture. The ties between polymer chains are called cross-links, and the process of cross-linking the polymer is the process of vulcanization. This term is used whether or not heat is required.

The silicone rubbers used for medical purposes contain fillers and vulcanizing agents, but they do not contain the wide variety of additives used in organic rubber compounding.

The medical-grade silicone rubbers can be divided into two categories: the heat-vulcanizing types and the room-temperature-vulcanizing types (commonly called RTV's). The latter can be further divided into those which vulcanize after the addition of a catalyst and those which vulcanize by reaction with water absorbed from the air.

THE HEAT VULCANIZING TYPES OF SILICONE RUBBER

There are three commonly used medical-grade, heat vulcanized silicone rubbers: Silastic 370, Silastic 372, and Silastic 373. They cover the hardness range from soft through medium to hard. In the raw state, compounds with equivalent composition are available under the nomenclature "Clean Room Stocks." They are MDX 4-4514, MDX 4-4515, and MDX 4-4516, respectively.

The filler used in these three compounds is a very pure, finely divided

silica with a particle size of about 30 mμ. Without this filler the silicone rubber would have insufficient strength. In general the more filler used, the harder is the resultant rubber.

Two types of polymers are used in these three stocks. The medium and hard grades are made from a polymer composed primarily of the dimethyl type but with very small amounts of methylvinyl siloxy units

$$
\left[
\begin{array}{c}
CH_3 \\
| \\
-Si-O- \\
| \\
C-H \\
\| \\
H-C-H
\end{array}
\right]
$$
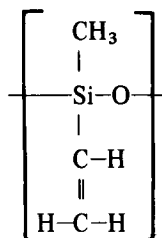
copolymerized with it. Such a stock is referred to as a methylvinyl/dimethyl silicone copolymer. This copolymer is used because the methylvinyl portion makes for a more efficient vulcanization, yielding a rubber with better properties.

Silastic 370 is made from a polymer that, in addition to the methylvinyl group, also contains a small per cent of methylphenyl siloxy units

$$
\left[
\begin{array}{c}
Me \\
| \\
-Si-O- \\
| \\
\bigcirc
\end{array}
\right]
$$
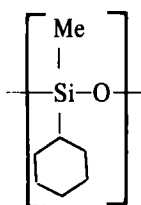
The presence of this group enables the compounder to make a soft rubber with better properties than if this were not present. The polymer is therefore a phenylmethyl/vinylmethyl/dimethyl silicone copolymer. All these polymers, however, contain a great preponderance of dimethyl siloxy units.

The vulcanizing agent in all three compounds is dichlorobenzoyl peroxide. The mechanism by which this vulcanizing takes place is worthy of description, since it varies considerably from the mechanism of vulcanization of most organic rubber. When the plastic mass containing the polymer, filler, and vulcanizing agent is heated, the vulcanizing agent breaks down, forming free radicals:

$$
\begin{array}{cc}
O & O \\
\| & \| \\
\end{array}
$$

C–O–O–C

Cl · Cl → 2 · Cl + 2CO$_2$
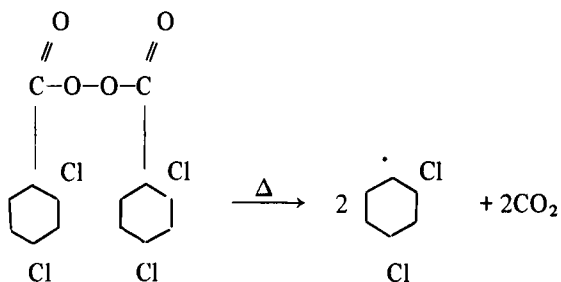
The dichlorophenyl free radical then will add on to the vinyl group on the polymer:

CH$_3$
|
–Si–O–
|
· C–H
|
H–CH
| Cl

Cl
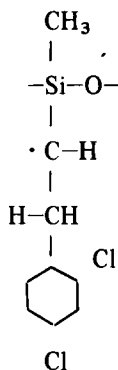
When this contacts a methyl group on a neighboring polymer chain, it pulls off a hydrogen.

CH$_3$ CH$_3$
| |
–Si–O–   →   –Si–O–
| |
CH$_3$ HĊH
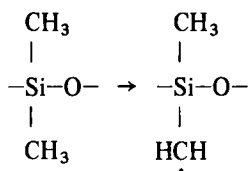
Simultaneously, the dichlorophenyl group is removed from the other polymer chain:

$$
\begin{array}{c}
\underset{|}{CH_3} \\
-Si-O- \\
| \\
\cdot CH \\
| \\
H-C-H
\end{array}
\rightarrow
\begin{array}{c}
\underset{|}{CH_3} \\
-Si-O- \\
| \\
H-C-H \\
| \\
H-C-H \\
\cdot
\end{array}
+
$$
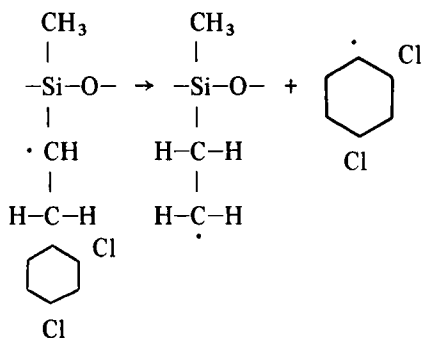
There is now an ethyl side group on one polymer chain and a methyl on another, both with an unsatisfied valence. These combine and form a propyl cross-link between the two polymer chains:

$$
\begin{array}{c}
CH_3 \\
| \\
-Si-O- \\
| \\
H-C-H \\
| \\
H-C-H \\
| \\
H-C-H \\
| \\
-Si-O- \\
| \\
CH_3
\end{array}
$$
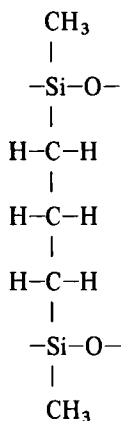
The dichlorophenyl free radical has been regenerated and is available for further cross-linking. There are, of course, other reactions that take place, such as methyl-methyl cross-links, but the above is thought to be the dominant reaction.

It can be seen that vulcanization has been accomplished without the vulcanizing agent becoming a part of the resultant rubber, as is the case when organic rubber is vulcanized with sulfur. The peroxide does its job of cross-linking, and then is fugitive, its break-down products being driven off during the heat cure that silicone rubber undergoes following the vulcanizing step. Thus a vulcanized and cured medical grade silicone

rubber of the heat vulcanizing type ultimately contains only the silicone polymer and the silica filler. Properties typical of those which can be expected when these stocks are correctly vulcanized and cured are listed in Table 2.

ROOM-TEMPERATURE-VULCANIZING (RTV) SILICONE RUBBER

There are two major types of silicone rubbers that do not require heat for vulcanization: the two-component types and the one-component types. The two-component types require that a catalyst be mixed into the base to bring about vulcanization. The one-component types do not require the mixing in of a catalyst, for ambient water causes the vulcanization to occur.

THE TWO COMPONENT RTV

The two components of these materials are the catalyst and the base. The latter is a compound of a fluid silicone polymer mixed with filler and a material designed to act as a cross-link.

Because of the necessity of mixing in a catalyst, the viscosity of the polymer used must be low enough to permit easy stirring. Also, the fillers used must not thicken the mixture too greatly. These facts militate against a strong, tear resistant, silicone rubber. As a consequence, most of the two-component RTV silicone rubbers are relatively weak, with low tear strength. They find their widest use in such static applications as potting and encapsulating.

The fillers used in these compounds are generally diatomaceous earths. They serve to give more strength to the polymer than it would have were there no filler added.

There are many different catalysts for the RTV's, all in the field of the organo-metallic compounds, but the only one thus far found satisfactory for medical application is stannous octoate:

$$\text{Sn}\left[\begin{array}{l}
\overset{\displaystyle CH_3}{\underset{\displaystyle |}{}}\\
\overset{\displaystyle O}{\overset{\displaystyle \|}{}}\ \overset{\displaystyle CH_2}{\underset{\displaystyle |}{}}\\
O-C-C-CH_2-CH_2-CH_2-CH_3\\
\underset{\displaystyle H}{\underset{\displaystyle |}{}}
\end{array}\right]_2$$
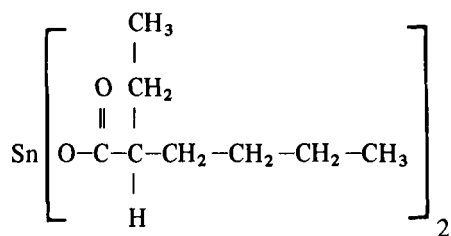
Table 2. Typical Properties of Heat Vulcanizing Medical Grade Silicone Rubber[a]

Property	Test method	Soft	Medium	Firm
Color	—	Translucent	Translucent	Translucent
Specific gravity	—	1.12	1.14	1.23
Durometer hardness, Shore A	ASTM D676	25	50	75
Tensile strength, psi	ASTM D412	850	1200	1000
Elongation %	ASTM D412	600	450	350
Die B tear strength, pi	ASTM D624	70	75	75
Brittle point, °F	ASTM D746	-175	-100	-100
Electric strength,[b] V/mil	ASTM D149	500	540	540
Dielectric constant at 10^2, cps	ASTM D150	2.91	2.8	2.8
Dielectric constant at 10^5, cps		2.90	2.8	2.8
Dissipation factor at 10^2, cps	ASTM D150	0.0006	0.0008	0.0008
Dissipation factor at 10^5, cps		0.0006	0.0009	0.0009

[a] All physical and electrical properties measured on 1/8 in. thick samples molded 5 min at 240°F and oven cured 1 hr at 480°F.

[b] Continuous voltage rise, 1/4 in. electrodes, silicone rubber samples 1/16 in. thick.

Table 3. Typical Properties of Silastic 382 Medical Grade Elastomer

Property	Test method	
Viscosity, centipoises		50,000
Before Catalyzing		
After Vulcanizing for 24 Hr at 77°F		
Color		White
Specific gravity		1.13
Durometer hardness, Shore A	ASTM D676	43
Tensile strength, psi	ASTM D412	400
Elongation, %	ASTM D412	160
Die B tear strength, pi	ASTM D624	25
Brittle point, °F	ASTM D746	-100
Shrink, linear, %		
after 3 days at 77°F		0.4
after 6 days at 77°F		0.6
after 14 days at 77°F		0.7
Water absorption, %, after 7 days immersion at 77°F		0.4
Thermal conductivity, cal/cm °C sec		0.525×10^{-3}
Volume coefficient of thermal expansion/°C (0 to 100)		7.50×10^{-4}

In the pure state this material can cause reddening of the skin and is damaging to the eye. Medical-grade RTV silicone rubber vulcanized with it and implanted in the tissue, however, shows no more tissue reaction than the other medical-grade silicones. On the other hand, the same RTV base when vulcanized with some of the other common industrial grade RTV catalysts, such as dibutyl tin dilaurate, and implanted subdermally will show severe tissue reaction. It is this type of problem that prompt us to warn repeatedly against the use of industrial-grade silicones in medical applications.

The process of vulcanization of the two component RTV's is as follows: The polymer used has a high degree of hydroxy end-blocking:

$$
\begin{array}{ccccc}
CH_3 & & CH_3 & & CH_3 \\
| & & | & & | \\
HO-Si-O & - & Si-O & - & Si-OH \\
| & & | & & | \\
CH_3 & & CH_3 & & CH_3 \\
& & & x &
\end{array}
$$
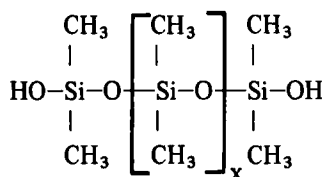
The cross-linking between these polymer chains is accomplished by a material such as propyl orthosilicate:

$$Si(OCH_2-CH_2-CH_3)_4$$
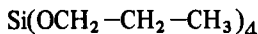
When a catalyst is stirred into a mixture composed of this and a hydroxy end-blocked silicone polymer, the hydroxyl on the end of the polymer reacts with the alkyl group, forming an alcohol. The polymer chain then attaches to the silicate as shown on the following page. Thus the network necessary for a material to have rubbery properties is formed. Typical properties for Silastic 382 medical-grade elastomer, the most widely used medical grade RTV, are found in Table 3.

THE ONE-COMPONENT RTV'S

The one-component RTV's were developed originally as adhesives and are often classified under this term. They will adhere well to silicone rubber and to many other materials.

$$
\begin{array}{c}
CH_3 \\
| \\
CH_2 \\
| \\
CH_2 \\
| \\
O \\
\end{array}
$$

$$
CH_3 \qquad\qquad\qquad CH_3 \qquad\qquad\qquad\qquad CH_3
$$

$$
-O-Si\!\!-\!\!\big[\,OH \;\; CH_3CH_2CH_2\,\big]\!\!-\!\!O-Si-O\!\!-\!\!\big[\,CH_2CH_2CH_3 \;\; OH\,\big]\!\!-\!\!Si-O-
$$

$$
CH_3 \qquad\qquad\qquad\qquad\quad O \qquad\qquad\qquad\qquad\qquad CH_3
$$

$$
\begin{array}{c}
CH_2 \\
| \\
CH_2 \\
| \\
CH_3 \\
\quad CH_3 \\
\quad | \\
OH \;\; Si-O- \\
\quad | \\
CH_3
\end{array}
$$
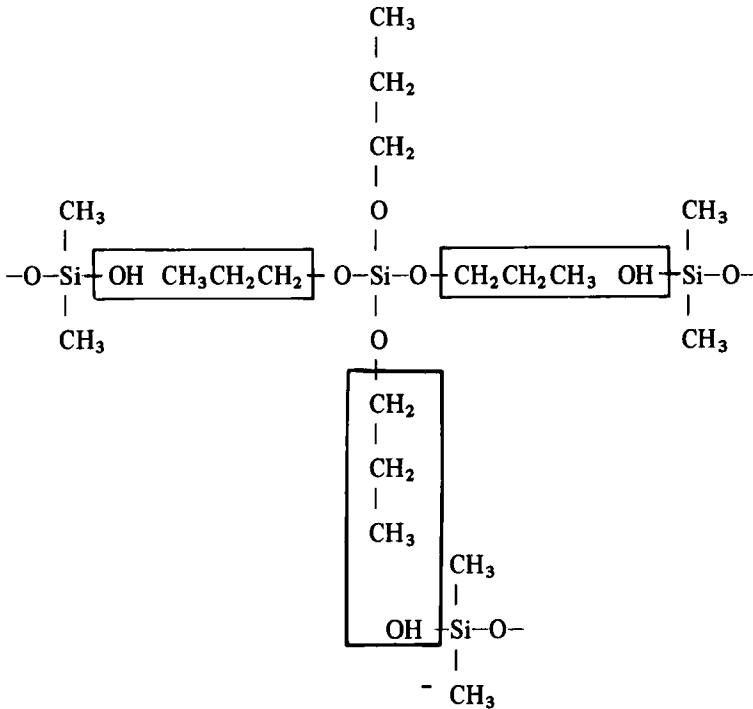
The silicone polymer used in these is a relatively low molecular weight hydroxy end-blocked polymer. The material used to cross-link the polymer is methyl triacetoxy silane:

$$
CH_3-Si-\left(O-\overset{\displaystyle O}{\overset{\|}{C}}-CH_3 \right)_3
$$
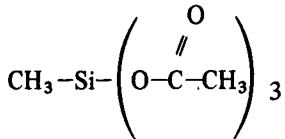
The silicon-oxygen-carbon bond is easily hydrolyzed by water. Thus, when water contacts the triacetoxy silane, acetic acid is formed, leaving a hydroxyl from the water in place of the acetoxy groups:

$$
\text{HO}\;\big|\;\text{H}\;\;\text{CH}_3-\overset{\displaystyle O}{\overset{\|}{C}}-O\;\big|\!\!-\!\!-\overset{\displaystyle \underset{|}{CH_3}}{Si}\!\!-\!\!-\big|O-\overset{\displaystyle O}{\overset{\|}{C}}-CH_3\;\;\text{H}\;\big|\;\text{OH}
$$

$$
\begin{array}{c}
O \\
| \\
C=O \\
| \\
CH_3 \\
\\
H \qquad OH
\end{array}
$$
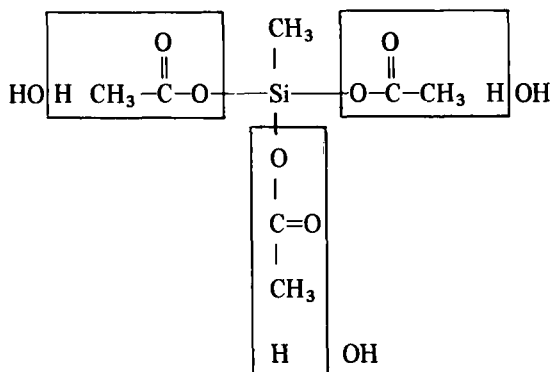
Methyl silanes with multiple hydroxyl groups, however, are very unstable, and these will condense with the hydroxy end-blocked silicone polymer, thus creating longer polymers and at the same time crosslinking them:

$$
-\overset{\displaystyle \underset{|}{CH_3}}{\underset{CH_3}{Si}}\!\!-\!\!\big|\text{OH}\;\;\text{H}\big|O-\!\!-\overset{\displaystyle \underset{|}{CH_3}}{\underset{\underset{H}{O}}{Si}}\!\!-\!\!O\big|\text{H}\;\;\text{OH}\big|\!\!-\overset{\displaystyle \underset{|}{CH_3}}{\underset{CH_3}{Si}}\!\!-
$$

$$
\text{HO}\big|\!\!-\overset{\displaystyle \underset{|}{CH_3}}{\underset{CH_3}{Si}}\!\!-
$$
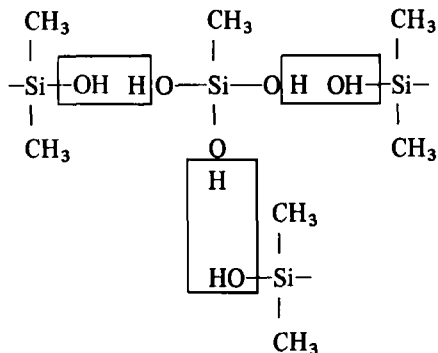
The filler used in these compounds is similar to that used in the heat vulcanizing silicone. Unvulcanized medical-grade silicone adhesive is a soft, nonflowing paste, resembling white Vaseline. Properties typical of what can be obtained with Silastic Medical Adhesive Type A, the most commonly used medical-grade silicone adhesive, are found in Table 4. Because of the necessity for water to penetrate the mass, full cure generally requires about 24 hr. There is about 6% acetic acid given off during this cure (vinegar contains about 4% acetic acid). Because of lower hardness and higher elongation, the tear strength of Medical Adhesive Type A is superior to Silastic 382 medical-grade elastomer, and the material gives the impression of having better tensile strength than is actually measured.

Table 4. Typical Properties of Silastic Medical Adhesive Type A

Property	Test method	
Color	–	Translucent
Specific gravity	–	1.12
Durometer hardness, Shore A scale	ASTM D676	28
Tensile strength, psi	ASTM D412	300
Elongation, %	ASTM D412	450

"MEDICAL GRADE"

The term "medical grade" is applied to those silicones that fulfill three requirements:

1) A long history of successful implantation in animals and humans.

2) Manufactured under pharmaceutically clean conditions.

3) Quality controlled for medical applications.

Some industrial silicones are known to be toxic when placed sub-dermally. Others may be satisfactory for medical use, but there are still pitfalls. Industrial-grade silicone materials are carefully compounded and quality controlled for specific end uses, and they perform their duties safely and adequately, but they are not intended for medical use. A stock designed for caulking windows might be tested and found satisfactory for implanting in the body, but a change in the formulation to make a better caulking compound could be catastrophic for the surgeon. For these reasons, it is well to use only those materials designed and tested with medical use in mind.

CONCLUSION

The rapid expansion of the technology of the silicones over the past quarter century has given the medical profession a new set of tools to work with. As a result, hundreds of thousands of persons now have

silicones implanted in their bodies, performing functions that only a short time ago were impossible. Future developments seem to be limited only by the ingenuity of the investigator.

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