

CHAPTER II

THEORY

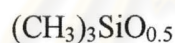
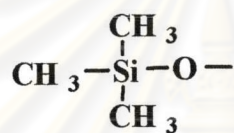
2.1 SILICONE RUBBER

2.1.1 Poly(dimethylsiloxane) [3]

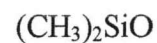
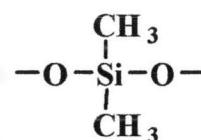
Nomenclature : $-[(CH_3)_2Si-O-]_n$

Shorthand notation for siloxane polymer units

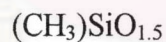
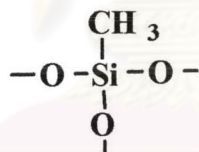
Formula:



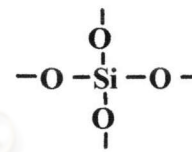
M (monofunctional)



D (difunctional)



T (Trifunctional)



Q (tetrafunctional)

Table 2.1 End-group and structure of siloxane polymer units

End group	Structure
Methyl	$(CH_3)_3Si-O-[(CH_3)_2Si-O-]_nSi(CH_3)_3$
Hydroxyl	$HO-(CH_3)_2Si-O-[(CH_3)_2Si-O-]_nSi(CH_3)_2-OH$
Vinyl	$CH_2=CH-(CH_3)_2Si-O-[(CH_3)_2Si-O-]_nSi(CH_3)_2-CH=CH_2$
Hydrogen	$H-(CH_3)_2Si-O-[(CH_3)_2Si-O-]_nSi(CH_3)_2-H$
None	$[(CH_3)_2Si-O-]_3$; cyclic trimer
Methyl	$[(CH_3)_2Si-O-]_3SiH$

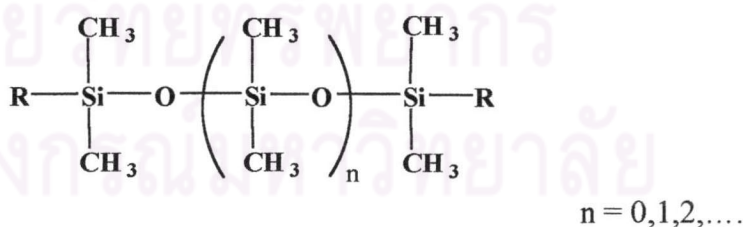
Table 2.2 Product form and properties

Form	Structure and properties
Fluids	Linear polymer. Liquid at low molecular weights and solid gum at high molecular weights
Elastomers	Cross-linked solids. Reinforcement necessary for property performance
Resins	Highly branched cross-linked solids or fluids

Table 2.3 Infrared characteristic absorption

Group	Absorption, wave number(cm^{-1})
$-\text{Si}(\text{CH}_3)_2-\text{O}-\text{Si}(\text{CH}_3)_2-$	2,905-2,960; 1,020; 1,090
$\text{Si}(\text{CH}_3)_3$	2,905-2,960; 1,250; 840; 765
$\text{Si}(\text{CH}_3)_2$	2,905-2,960; 1,260; 855; 805
$\text{Si}-\text{CH}_3$	2,905-2,960; 1,245-1,275; 760-845
$\text{Si}-\text{H}$	2,100-2,300; 760-910
$\text{Si}-\text{OH}$	3,695; 3,200-3,400; 810-960
$\text{Si}-\text{CH}=\text{CH}_2$	1,590-1,610; 1,410; 990-1,020; 940-980

2.1.2 Reactive End Groups

**Figure 2.1** Types of silicone rubber

R group is: methyl (CH_3) in MQ, vinyl ($\text{CH}=\text{CH}_2$) in VMQ
 phenyl (C_6H_5) in PMQ, trifluoropropyl ($\text{CH}_2-\text{CH}_2-\text{CF}_3$) in FMQ
 PVMQ rubbers have phenyl, vinyl and methyl groups.
 FVMQ rubbers have trifluoropropyl, vinyl and methyl groups.

Chemically, silicone rubbers are substituted polysiloxanes (Figure 2.1). They are denoted generically by the letter Q. The letter MQ denote the basic silicone rubbers that have only methyl substituents in the polysiloxane chain. By replacing small amounts of these methyl groups with other groups, significant variations in properties can be achieved. The presence of the vinyl groups in VMQ improves vulcanization rate and compression set resistance. The phenyl groups in PMQ and PVMQ improve low-temperature flexibility and resistance to high-energy radiation. The addition of trifluoropropyl groups to the polymer chain results in a special type of silicone rubbers commonly known as fluorosilicone rubbers (FMQ and FVMQ). The vulcanizates of these rubbers exhibit excellent resistance to oils and many solvents while retaining the basic properties of silicone elastomers. [4]

2.2. GENERAL SILIOCONE RUBBER TECHNOLOGY [5]

2.2.1 Manufacturing and Polymerization

Figure 2.1 shows the all-methyl-substituted silicone polymer polydimethyl-siloxane. Polymers of either this type or one containing a small amount (e.g., less than 0.5 mol %) of vinyl substitution for methyl groups are the most widely used polymers in silicone elastomer technology. The methyl group substitution is the most easily accomplished and can be made from quartz, coke, chlorine and water. A flow diagram for the manufacture of polydimethylsiloxane is given in Figure 2.2 The coke is used to reduce silicon in quartz to metallic silicon, which can then be reacted with methyl chloride to form a mixture of silanes, $\text{Cl}_{4-n}(\text{CH}_3)_n\text{Si}$, where n can be 0, 1, 2, 3 or 4. The dimethyldichlorosilane is separated from the mixture of substituted cyclic siloxanes, $[(\text{CH}_3)_2\text{SiO}]_x$, for use in preparing polymers. Silicone rubbers can be divided into three groups: heat-vulcanizable solid rubbers, heat-vulcanizable liquid silicone rubbers (LSR) - designed for the automated production of molded parts and room temperature vulcanizing rubbers (RTV) - usually flowable liquids supplied in a “ready to use” form for such applications as building sealants, encapsulation, coating and flexible molds.

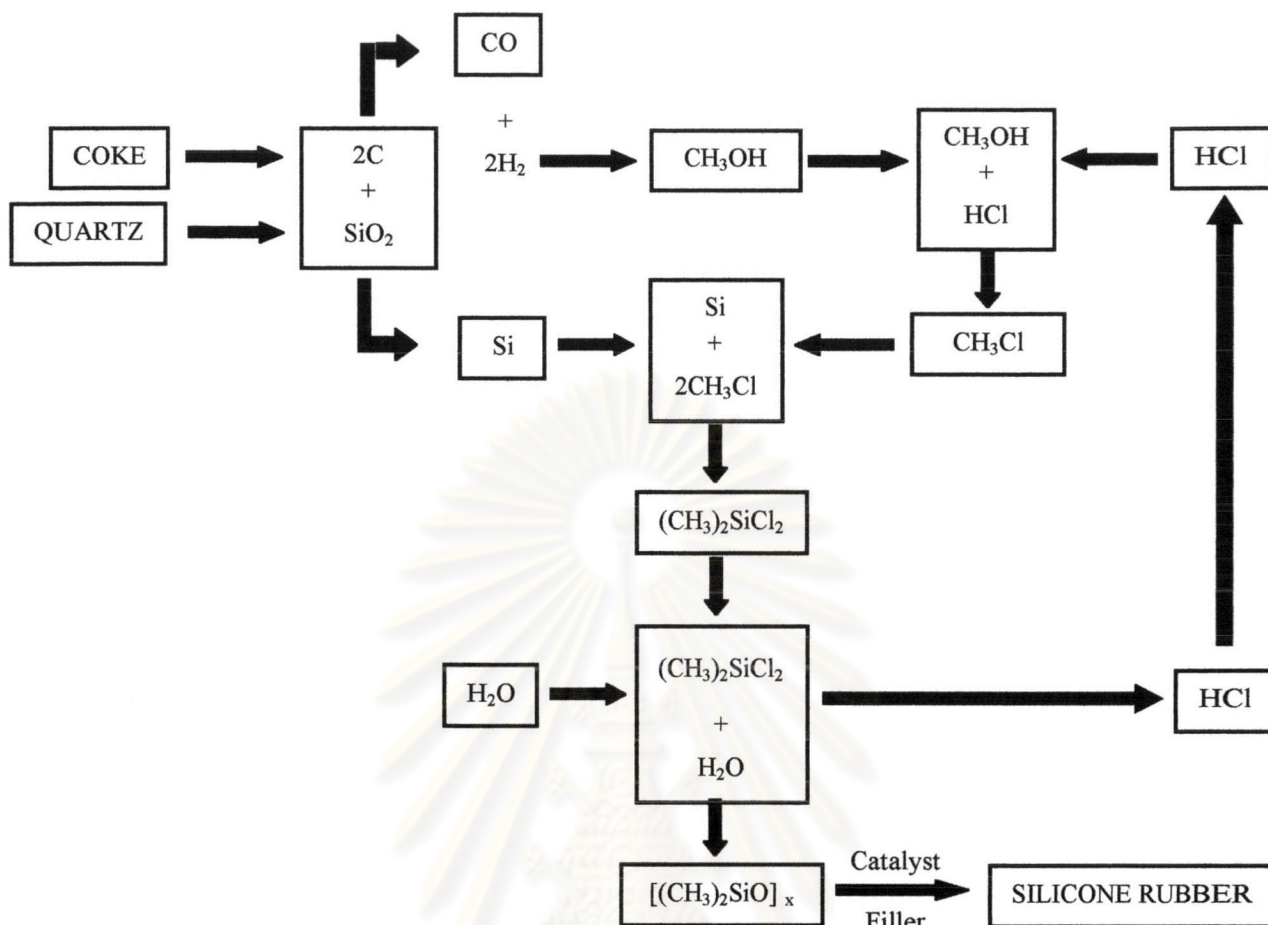


Figure 2.2 Polydimethylsiloxane manufacturing. (Polmanteer, 1981.)

The average number of siloxane units in the polymer is controlled to best satisfy the properties desired from a given composition. The polymers used in high-consistency compositions usually contain from 3,000 to 10,000 siloxane repeating units, while polymers used in room-temperature (RTV) and liquid silicone rubber (LSR) compositions contain between 50 and 2,000 siloxane repeating units.

The normal procedure for preparing high-molecular-weight polydimethylsiloxane is to control the hydrolysis of the dimethyldichlorosilane to form cyclic siloxane intermediates, which are then polymerized via a ring-opening reaction. A wide variety of catalysts may be used to polymerize the cyclic siloxanes. These catalysts include proton acids, Lewis acids, acid clays and many bases. The principle cyclic used in preparing high polymers is the tetramer, which may be polymerized with alkaline catalyst as shown in Figure 2.3. This is an equilibrium

reaction such that a certain ratio between linear and cyclic species is maintained at equilibrium.

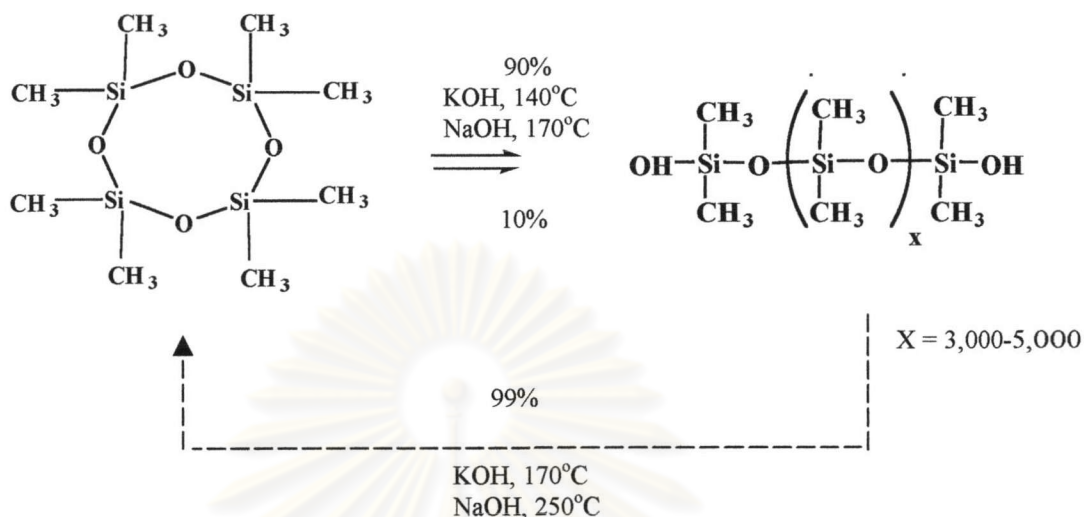
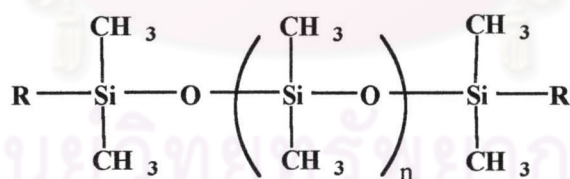


Figure 2.3 Polymerization of cyclic dimethylsiloxanes. (Polmanteer, 1981.)

Silicone oil is a linear polymer whose chains contain between 2-1,000 siloxane repeating units as shown in structure below. Silicone oils have a very wide temperature range of application and excellent oxidation and thermal stability. As would be expected, silicone elastomers tend to swell and soften excessively in silicone oils, particularly at high temperatures.



$$n = 2 - 1,000$$

In general, silicone oils cause hardly any swell, but they extract soluble components (particularly plasticizers) from the elastomers, causing them to shrink. The effect is most severe with low-viscosity silicone oils at high temperatures. Plasticizers or softeners are small molecule that are added to polymer to lower its glass transition temperature. They must be completely compatible with the crude rubber and other compounding ingredients because incompatibility will result in poor processing. Plasticizers are incorporated for various purposes: as an extender to make

the final product less expensive, a processing aid to facilitate the manufacturing operations of the compounded rubber or a modifier of certain vulcanizate properties.

2.2.2 Reinforcement

It is necessary to reinforce the siloxane polymers used in elastomer applications. This is the case since the typical linear diorganosubstituted polysiloxanes used in commercial silicone elastomers are amorphous, flowable polymers at room temperature and have only approximately 0.34 MPa tensile strength when crosslinked. It is indeed fortunate that the strength can be increased by the addition of special silica fillers. Figure 2.4 by the work of Polmanteer and Lentz show that the strong bonding of the silica filler to the polymer is related to the combination of chemical and physical bonds. The physical bonds are strong and include both Van der Waals forces and hydrogen bonding of silica silanols with polymer silanols and the polydimethylsiloxane chain oxygen atoms.

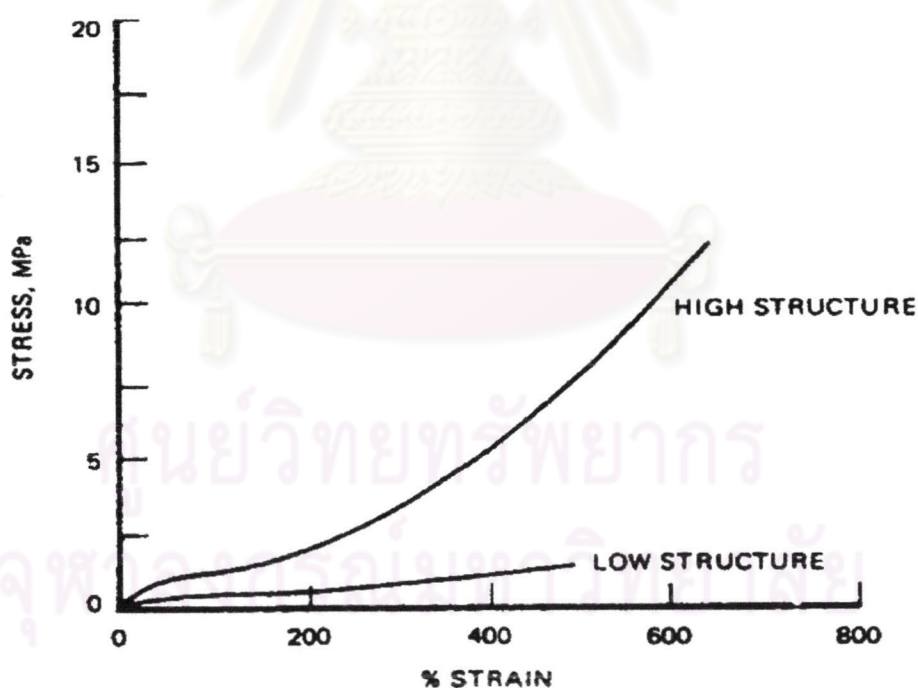


Figure 2.4 Stress-strain curves to rupture for silicone elastomers filled with low and high structure silica. (Polmanteer, 1981)

Most commercial high-consistency silicone elastomers contain a combination of several fillers to give a specified combination of properties for a particular type of application. For example, iron oxide and other metal oxides are often used in small quantities to improve such properties as thermal stability and compression set or to impart a particular color to the elastomer. Extending fillers are often used to improve the processing properties and reduce the cost of the elastomer. Typically, lower-consistency silicone rubber compositions such as those used for RTVs and LSRs contain lower levels of fillers than high-consistency rubber compositions.

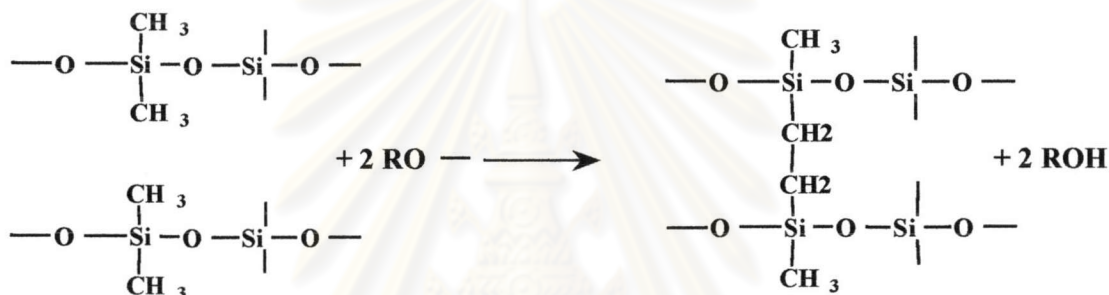
2.2.3 Vulcanization

Crosslinks are junctions of polymer strands in a three-dimensional network. Vulcanized silicone rubber may have 100-400 repeating units. In addition to chemical crosslinks, there are chain entanglements that behave as effective crosslinks. A soft gel forms when there are an average of one intermolecular crosslink per two weight-average molecules (one share of a cross-link per weight-average molecule). Increased crosslinking gives an elastomer with progressively increased stiffness until elasticity is lost when there are only a few chain atoms between cross-links. We are concerned both with crosslinks formed by chemical bonding, which usually are permanent, and with crosslinks formed by physical bonding, including entanglements between polymer chains, which may be temporary. Chemical crosslinks may be formed by bonds between established polymer molecules, or by branching during the polymerization process. Crosslinking affects many mechanical properties of polymer. As crosslinking increases over the range of practical interest, the ultimate properties of tensile strength and tear strength generally pass through maxima while the strain at failure and degree of solvent swelling both decrease. Other properties such as the dielectric loss factor and, to some extent, the diffusion coefficient of elastomer networks also depend on the extent of crosslinking. Process and environmental conditions that affect the extent of crosslinking clearly affect all of these properties. The chemical routes to be described for the vulcanization of silicone elastomers will be confined to the primary technologically important systems: (1) elevated temperature cures (2) room temperature vulcanizing (RTV) mechanisms.

Elevated temperature cures

Peroxides

The most commonly used vulcanizing agents for the heat curing silicone rubbers are organic peroxides. Used in very low concentration, the action of the peroxides appears to be that free radicals, produced as the peroxides reach their decomposition temperature, capture hydrogen atoms from methyl groups of adjacent linear molecules, thus causing cross linking. The silicone gum becomes a true resilient rubber as a consequence:



The most popular of the organic peroxide curing agent is 2,4-dichlorobenzoyl peroxide. It has the lowest vulcanization temperature combined with the highest rate of vulcanization. Because its decomposition products have a very low vapor pressure, external pressure is not required to prevent porosity.

Benzoyl peroxide is another low temperature catalyst that may be used to vulcanize all types of silicone and fluorosilicone compounds. It has fewer tendencies to scorch than 2,4-dichlorobenzoyl peroxide. Consequently, it is better in molding very thin sections. However, because of its tendency to generate volatile gas, it is not as good for hot air vulcanization. It is used in continuous steam vulcanization, the standard method for vulcanizing wire and cable coating.

Hydrosilation

Crosslinking can also be accomplished with a hydrosilation reaction whereby a Si-H group will add to a vinyl group. A platinum catalyst such as chloroplatinic acid is normally used in this reaction (Figure 2.5)



Figure 2.5 Hydrosilation reaction. (Polmanteer, 1981)

A low molecular weight silicone molecule having several Si-H groups in it is mixed with a silicone polymer having several vinyl groups attached to silicon atoms. The platinum catalyst causes the necessary addition reactions to occur, thus forming a crosslinked polymer network. These reactions are accelerated by heat but also occur readily at room temperature. Hence, this crosslinking method can be used either at elevated temperature or at room temperature. Since this is an addition reaction, no volatiles are generated when the crosslinks are formed. This hydrosilation reaction is particularly important and widely used in LSR compositions.

Room-Temperature Vulcanization

Room-temperature vulcanization is normally used with low consistency silicone elastomers. They are now available in a range of viscosities varying from thin and easily poured liquids. Cure times can be controlled over a wide range and in many applications curing is accomplished at elevated temperatures, sometimes in a matter of seconds. Moreover, room-temperature vulcanization can be divided into two groups:

One-Part Systems

One-part cure systems can be placed in one package and remain non-crosslinked. When the material is exposed to a reactant, normally from the atmosphere, a sequence of reactions takes place leading to the formation of crosslinks. Moisture in the atmosphere is the most common reactant of one-part RTVs. Atmospheric moisture first reacts with hydrolyzable groups attached to silicon.

(Figure. 2.6). The silanol formed can condense with either another silanol group or a hydrolyzable group on silicon, thus forming a Si - O - Si linkage and a condensation by-product (Figure 2.7). In most instances these by-products are acidic or basic enough to act as catalysts for the crosslinking (Si - O - Si) forming reaction. The two generalized reactions just described can be applied to a wide variety of specific hydrolyzable groups. Suitable hydrolyzable groups such as: acyloxy, oxime, alkoxy or amino. Although a specific catalyst may be applicable to only a certain type of RTV, examples of some of the catalysts include fatty acid salts of metals such as tin and lead, amines, amine salts, titanates and aluminates.



where OX = hydrolyzable groups

Figure 2.6 Hydrolysis reaction.

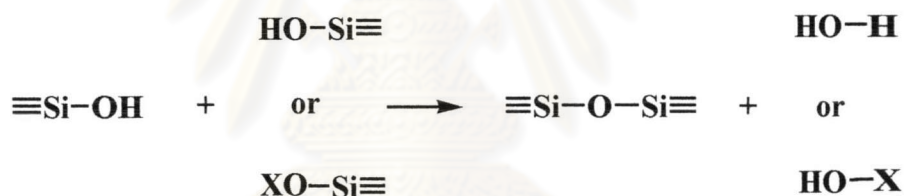


Figure 2.7 Condensation reaction.

Two-Part Systems

Since this system cures readily, even at room temperature, when the three necessary components, SiH-containing crosslinker, Si - Vi- containing polymer and platinum catalyst, are mixed together, it is referred to as a two-part system. In other words, one part contains two components and the two parts contain three necessary components. When vulcanization is desired, the two parts are mixed together. Hence, systems involving the mixing of two components followed by vulcanization are referred to as two-part curing systems. Condensation reactions can be used in two-part RTV systems. The reactions normally involve a functional chain end and a polyfunctional compound as shown in Figure 2.8

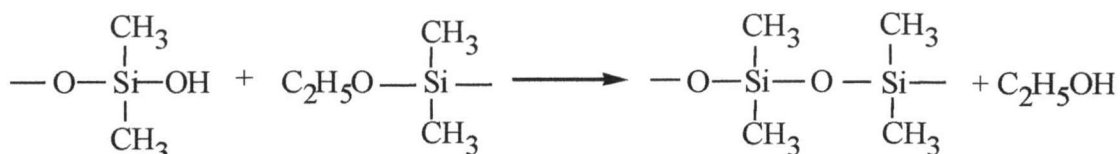


Figure 2.8 End group reaction (lengthens molecule)

For example, a convenient method is to react a silanol chain end with a silicate such as polyethylsilicate (reaction shown in Figure 2.9) This cure system was filed with the U.S. Patent in 1954). This is simple condensation reaction catalyzed with fatty acid salts of tin, lead, cobalt, etc., giving a siloxane linkage and ethanol. Thus, the silicate, being polyfunctional, can react with several chain ends to tie the network together. The catalyst necessary for this reaction is normally not added until it is desired to have the crosslinking start. Cure does not require atmospheric moisture, hence deep section cures are possible. However, it is preferable for the alcohol by-product formed to rapidly diffuse out of the system so as not to retard the crosslinking reactions via silanol-ethanol reactions.

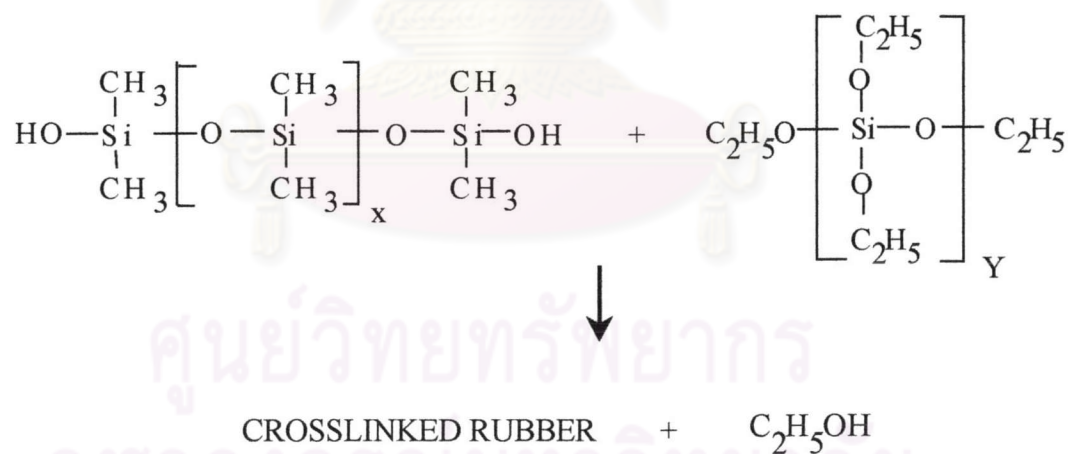


Figure 2.9 Condensation crosslinking chemistry. (Polmanteer, 1981)

2.2.4 Vulcanizing Agents

Vulcanization is the process by which the elastomer molecules become chemically crosslinked to form three-dimensional structures having dimensional stability. The effect of vulcanization on compound properties is shown in Figure 2.10

Vulcanizing agents affect the rate of vulcanization, crosslink structure and final properties.

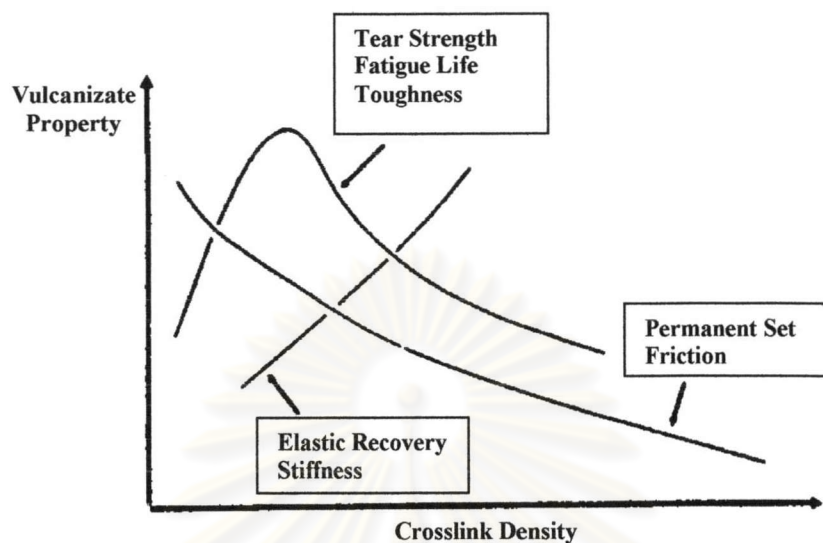


Figure 2.10 Vulcanizate properties as a function of the extent of vulcanization (Polmanteer, 1981)

2.2.5 Influence of Crosslink Density

Mechanical properties of an elastomer depend strongly on crosslink density. Modulus and hardness increase monotonically with increasing crosslink density, and the material becomes more elastic. Fracture properties, such as tear and tensile strength, pass through a maximum as crosslinking is increased. The effect of a few crosslinks is to increase the molecular weight, creating branched molecules and a broader molecular weight distribution. It is more difficult for these branched molecules to disentangle and hence, strength increases. As crosslinking is increased further, the gel point is eventually reached when a three-dimensional network forms. Some chains may not be attached to the network, but the whole composition no longer dissolves in a solvent. A gel cannot be fractured without breaking chemical bonds. Thus, strength is higher at the gel point, because chemical bonds must be ruptured to create fracture surface. However, strength does not increase indefinitely with more crosslinking.

When an external force deforms an elastomer, part of the input energy is stored elastically in the chains and is available as a driving force for fracture. The remainder of the energy is dissipated through molecular motions into heat, and in this manner, is made unavailable to break chains. At high crosslink levels, chain motions become restricted, and the “tight” network is incapable of dissipating much energy. This results in relatively easy, brittle fracture at low elongation. Elastomers have an optimum crosslink density range for practical use. Crosslink levels must be high enough to prevent failure by viscous flow, but low enough to avoid brittle failure.

2.3 GELATION AND NETWORK FORMULATION [6]

A characteristic feature during network formulation is the presence of a critical transition called gelation, which involves an abrupt change from a liquidlike to a solidlike behavior. Figure 2.11 illustrates the evolution of (zero-shear) viscosity, elastic modulus and fraction of soluble material (sol fraction), as a function of the conversion of reactive groups.

For conversions lower than x_{gel} the average molecular mass of the polymer exhibits a continuous increase. Gelation occurs when one of the growing molecules reaches a mass so large that it interconnects every boundary of the system. A similar way to describe this critical transition is by stating that gelation is defined by the percolation of the giant macromolecule throughout the system.

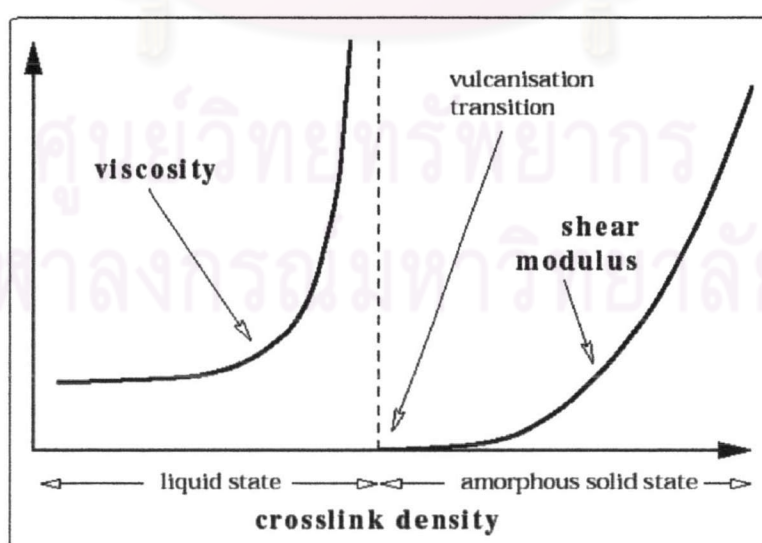


Figure 2.11 Evolution of physical properties of the thermosetting polymer as a function of conversion of reactive groups [7]

Dynamic mechanical measurements describe both the liquid and solid states. A freely oscillating torsion pendulum can be used to provide shear moduli data of solid specimens versus temperature or time. During such experiments, storage $G'(\omega)$, and loss $G''(\omega)$ shear moduli and their ratio, the loss factor $\tan\delta(\omega)$, are obtained:

$$G^*(\omega) = G'(\omega) + iG''(\omega)$$

$$\tan \delta = G''/ G'$$

Three typical regions are observed during cure (Matejka, 1991)

(a) The pregel region is characterized by an increase in the loss modulus, G'' , corresponding to the increase of the real part of dynamic viscosity due to the increasing molar mass of the thermosetting polymer. The storage modulus, G' , is very low and tends to zero at low frequencies. In this region the loss modulus, G'' , is higher than the elastic modulus (G'), and the loss factor, $\tan \delta > 1$.

(b) The “critical region” begins with a sudden increase in the storage modulus, G' , by several orders of magnitude. At the intersection of the $G'(t)$ and $G''(t)$ curves, $\tan \delta = 1$. After the intersection point, G' becomes higher and $\tan \delta$ becomes less than 1. The viscous properties are dominant in the liquid state. For this reason, the $G' - G''$ crossover ($\tan \delta = 1$) was firstly identified as the gel point (Tung and Dynes, 1982).

(c) Finally, in the postgel region, a slow increase in G' that levels off in the final stages of the reaction is observed; $\tan \delta < 1$ for the fully cured rubbery network. Additional experiments show that the stoichiometric mixture has the highest final modulus and the lowest final loss factor ($\tan \delta$) because it forms the most perfect network, with the highest crosslink density.

2.4 PHYSICAL AND MECHANICAL PROPERTIES [8]

2.4.1 The Measurement of Physical Properties

The physical properties of silicones are useful for their identification, determination of purity and characterization of structure. In general the same methods used to measure physical properties of nonsilicone materials can be used for silicones. The two major difficulties in measuring physical properties of silicone compounds are first, it is sometimes difficult to obtain a pure sample and second, many of the common organosilicon monomers are reactive and must be handled with care to avoid contamination during routine transfers to the measuring apparatus.

2.4.1.1 Viscosity

The viscosity of organosilicon monomers is usually in the range 0.5-10 centistokes (cS) [viscosity (cS) = viscosity (cP)/density (g/cm^3)]. Values for polymers can range from < 1 cS to more than a million centistokes. Figure 2.12 shows the relationship of viscosity to molecular weight for the low molecular weight pure PDMS species, and for narrow molecular weight fractions of higher molecular weight polymers. The phenylmethylsiloxanes and fluorosilicone polymers have similarly wide viscosity ranges. The polymer viscosities are also affected by molecular weight distribution and by branching of polymer chains. Commercial fluids may contain a wide range of molecular weights resulting from the manufacturing process, or from blending of fluids of different viscosities.

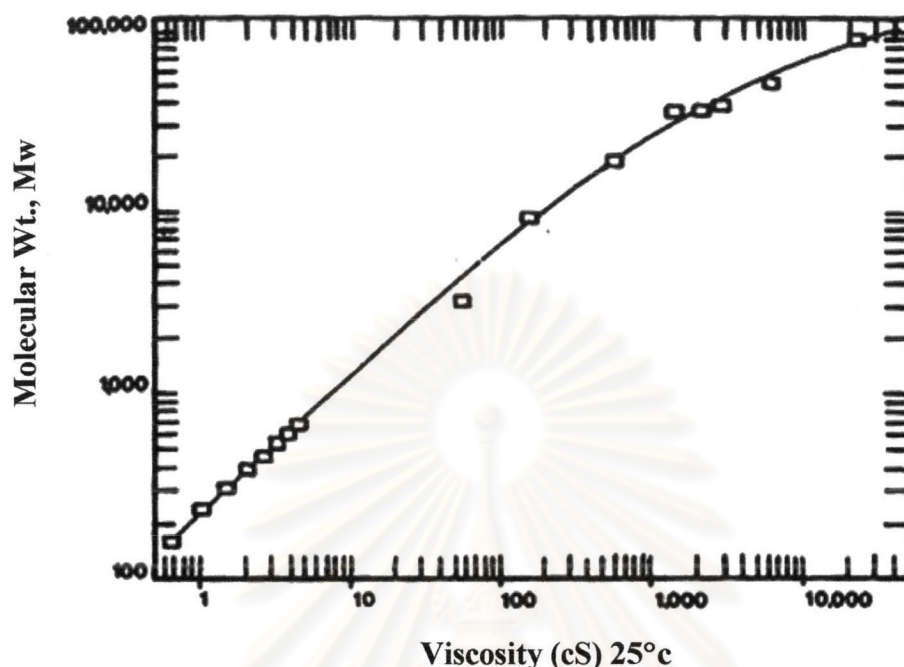


Figure 2.12 Relationship between viscosity of PDMS and weight-average molecular weight.

2.4.1.2 Molecular Weight

Important properties of a polymer usually are dependent on the molecular weights of the polymer molecules. The molecular weights, in turn, depend on the type and extent of the polymerization reaction, and upon subsequent processing such as the removal of components of low molecular weight (MW), or blending. For example, in silicone polymers, low-MW components often are observed. These include cyclic species that exist in equilibrium with the long-chain linear polymer. Average MW values become larger with an increase in the extent of the polymerization reaction, with a decrease in the concentration of chain-terminating species in the monomer composition, or with removal of low-MW cyclic and linear silicone species. The molecular weight distribution (MWD) of a polymer sample describes the relative numbers of molecules of all MW values.

Effect of MWD on Properties

Performance and processibility of silicones and other polymer products depend on combinations of their basic mechanical, thermal, interfacial, and diffusional properties. These properties, in turn, often depend on the MWD. The strong dependence of the viscosity and shear thinning of undiluted PDMS on \bar{M}_w . When \bar{M}_w exceeds about 35,000 for PDMS (its critical or entanglement MW) the viscosity dependence becomes even stronger. Here, the viscosity at low shear rate increases in proportion to \bar{M}_w because of the entanglement of polymer coils.

The viscoelastic responses also depend on MWD, as well as on the test temperature, time of deformation, and strain level. For polysiloxanes, relaxation of viscoelastic deformation is very rapid compared to organic polymers with their carbon chain backbones. Thus, for silicones of lower Mw, the deformation time must be short (high dynamic frequency) to capture elastic effects. Even for cured elastomers, the MWD before curing can be important. If the polymer ends are functionally active and form the cross-links, then the MWD before curing becomes the distribution of network chain lengths between cross-links, which determines the modulus of rigidity of the elastomer. If the ends are not functionally active, they become “dangling ends” which cannot support deformation stresses, thus lowering the modulus of the elastomer.

2.4.1.3 Service Lifetime [9]

Polysiloxane degradation temperatures, as measured by differential thermal analysis (DTA), are given in Table 2.4. The estimated service life of dimethylsilicone elastomers at elevated temperatures is shown in Table 2.5. Silicone elastomer compounds, however, contain a variety of ingredients and can be more stable toward degradation than the polymers without fillers and additives. Oxidation stability depends on the pendant organic groups. The decreasing order of stability is $C_6H_5 > CH_3 > C_2H_5 > C_3H_7 > C_2H_3$ (vinyl)

Table 2.4 Polysiloxane degradation temperatures

Silicone	Oxidation temperature In dry air, °C
ethylmethylsilicone	240
dimethylsilicone	290
methylphenylsilicone	375

Table 2.5 Estimated service life of silicone rubber

Temperature (°C)	Period (year)
90	40
121	10-20
150	5-10
200	2-5
250	0.25
315	0.04

Silicone rubber can burn, but the residue is siliceous rather than carbonaceous; it has some structural integrity and is a nonconductor of electricity. The limiting oxygen index for a typical formulation is 20. Flame-retardant versions with limiting oxygen index values as high as 40-50 is also available.

2.4.2 The Measurement of Mechanical Properties

Siloxanes are useful in such work because crosslink can be introduced and chain lengths determined in a carefully controlled manner by applying various cure chemistries. Stress-strain isotherms in elongations up to rupture behavior have been investigated.

Hookean elasticity [10]

The modulus is the most important strain mechanical property. It is the key indicator of the “stiffness” or “rigidity” of specimens made from a material. There are

three major types of moduli. The bulk modulus (B) is the resistance of a specimen to isotropic compression (pressure). The Young's modulus (E) is its resistance to uniaxial tension (being stretched). The shear modulus (G) is its resistance to simple shear deformation (being twisted).

Each type of modulus is defined in terms of the stress required to deform a specimen by a strain (γ) in the limit of deformation of the type quantified by that modulus. For example, Young's modulus is defined by equation 2.1

$$\sigma = E \cdot \gamma \dots \dots \dots (2.1)$$

Materials with a higher modulus (E) need more force or stress to obtain a given elongation than materials with a lower modulus. The elongation or strain is defined as equation 2.2

$$\gamma = \frac{(L - L_0)}{L_0} \dots \dots \dots (2.2)$$

L = length after stress has been applied

L_0 = initial length

Toughness is the result of the effects of molecular factors related to the nature of the materials. Attempts have been made to correlate these factors by means of a set of new quantitative structure-property relationships, which will be summarized later. Chemical crosslinks, which are a special type of molecular feature that can also affect the toughness in a significant manner.

Curve for typical silicone rubber is shown in Figure 2.13. It is a soft material. "Soft" refers to the fact that the initial slope is small, which means a low value of the modulus.

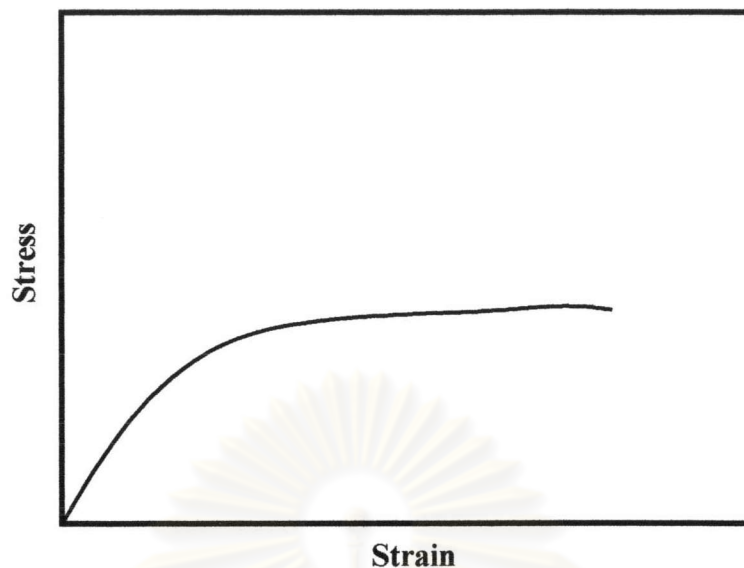


Figure 2.13 Stress-strain curve for typical silicone rubber [11]

2.5 SILICONES IN MEDICAL AND BIOLOGICAL APPLICATIONS

2.5.1 Medical Uses of Silicones

Because PDMS is relatively inert in the human body, medical grade elastomers, gels, and fluids are used for a wide variety of medical devices and therapeutic agents. Devices include implants, drug delivery systems, and adjunct devices such as rubber tubing for extracorporeal blood circulation, catheters, and the like. Therapeutic agents include antifatulent tablets as well as physiologically active materials.

Not all organosilicon materials are as inert as PDMS. Interest in the pharmacological and toxicological aspects of various organosilicon compounds has been strong. Such materials are of two categories: organosilicon compounds that are themselves bioactive; and conventional bioactive materials (drugs) that have been modified either by inclusion of a silicon bearing moiety, or by direct substituted of Si for C in the molecule. Even PDMS-based materials can evoke a “foreign body” tissue reaction under certain conditions. This reaction seems to be related to particle size and surface texture of the foreign body rather than its chemical constitution.

2.5.2 Mathematical Modeling of Human Breast

Many researchers have proposed imaging the stiffness distribution in breast tissue to enhance diagnosis of disease. They suppose that cancers are much stiffer than the surrounding tissue. In order to estimate the elastic modulus of the tissue from the punch indentation tests we will assume that the different types of tissues (tumor, normal glandular, fat etc.) can be modeled as homogeneous, and that their behavior in compression can be modeled as approximately isotropic. Further, we will make the assumption, as have other researchers[12], that the tissue is approximately incompressible.

In order to determine the elastic moduli of the tissue at various strain levels we need a mathematical model that relates the nominal stress and nominal strain developed during punch indentation tests to these moduli. This model must account for the apparent increase in stiffness that is due to the geometric non-linearity introduced by the thinness of the sample.

2.5.3 Mechanical Measurements of Human Breast Tissue

Few studies have been done to determine the mechanical properties of tissue in the breast, but average values of the Young's modulus have been calculated for fat, glandular tissue, and cancer tissue. Exponential curves (used in the past for several different tissue types) are used to describe the stress-strain curves obtained from uniaxial loading of breast tissue. The elastic modulus E_n for tissue type n is given as follows Table 2.6:

Table 2.6 Material properties of human skin [13]

Material properties	Values	Units
* Poisson ratio	0.49999	
Glandular tissue: $E_{gland}(\varepsilon_{gland}) = b_{gland} \cdot e^{m_{gland} \cdot \varepsilon_{gland}}$		N/mm ²
• b_{gland}	0.0151	N/mm ²
• m_{gland}	12.3	
Tumor tissue: $E_{tumor}(\varepsilon_{tumor}) = b_{tumor} \cdot e^{m_{tumor} \cdot \varepsilon_{tumor}}$		N/mm ²
• $b_{tumor}^{(1)}$	0.0379	N/mm ²
• $m_{tumor}^{(1)}$	19.9	
Fat exponential model: $E_{fat}(\varepsilon_{fat}) = b_{fat} \cdot e^{m_{fat} \cdot \varepsilon_{fat}}$		N/mm ²
• b_{fat}	0.00446	N/mm ²
• m_{fat}	7.4	
Updated fat model: $E_{fat}(\varepsilon_{fat}) = A \cdot \varepsilon_{fat}^2 + B \cdot \varepsilon_{fat} + C$		
• ε_{limit}	15.5	%
where $A = ((\varepsilon_{limit} \cdot m_{gland} - 1) \cdot b_{gland} \cdot e^{m_{gland} \cdot \varepsilon_{limit}} + b_{fat}) / \varepsilon_{limit}^2$ $B = ((2 - \varepsilon_{limit} \cdot m_{gland}) \cdot b_{gland} \cdot e^{m_{gland} \cdot \varepsilon_{limit}} - 2 \cdot b_{fat}) / \varepsilon_{limit}$ $C = b_{fat}$		
Skin model: $E_{skin}(\varepsilon_{fat}) = a_i$		
• $a_1(0 \leq \varepsilon_{skin} \leq 0.54)$	3.43	N/mm ²
• $a_2(0.54 < \varepsilon_{skin} \leq 0.68)$	28.89	N/mm ²
• $a_3(0.68 < \varepsilon_{skin} \leq 1)$	157.13	N/mm ²
• Skin thickness	1.0	mm
Notes: ⁽¹⁾ Ductal carcinoma		

* Poisson's ratio is related to elastic moduli K, the bulk modulus; G as the shear modulus; and E, Young's modulus, by the following. The elastic moduli are measures of stiffness. They are ratios of stress to strain. Stress is force per unit area, with the direction of both the force and the area specified