

# Room Temperature-Vulcanized Silicone Elastomer: Effect of Curing Conditions and the Nature of Filler on Mechanical and Thermal Properties

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## Synopsis

Linear poly(dimethylsiloxane diol) of about 650 D.P. was synthesized by hydrolytic condensation of dimethyldichlorosilane in a saturated solution of sodium chloride. The polymer was then compounded with various fillers, Cab-O-Sil, Dicalite, and titanium dioxide, and cured at room temperature in the presence of tin salt and tri- or tetrafunctional silane. The tensile strength and elongation of the unfilled rubber were found to be 0.8 kg/cm<sup>2</sup> and 320%, respectively. However, Dicalite White (100 phr)-reinforced elastomer showed a tensile strength of 40 kg/cm<sup>2</sup>. Crosslink density was determined from the swelling studies. Thermal aging at 150, 200, and 250°C was also studied.

## INTRODUCTION

Room temperature-vulcanized silicone elastomers have found widespread utility as biomaterials<sup>1-4</sup> which are successfully used in external prostheses for encapsulation and blood-compatible surface coatings. Tightly crosslinked RTV rubbers can be used in the electronic industry to pot delicate assemblies.<sup>5</sup> Molds for many applications are conveniently and economically made with the liquid silicone rubbers because they flow freely and reproduce the finest details of the pattern with practically no shrinkage. The mechanical strengths are normally lower than those of the corresponding heat cured silicones, but for many applications their convenience outweighs their reduced mechanical properties. A number of crosslinking agents<sup>6</sup> and catalysts<sup>7,8</sup> have been suggested for room-temperature vulcanization. The cure rate can be varied within wide limits by selecting the hydroxyl content of linear poly(dimethylsiloxane  $\alpha,\omega$ -diol), the nature and amount of the crosslinking agent<sup>9</sup> and the catalyst, temperature, moisture, and pH of the mixture.

The present work is concerned with the use of various crosslinking agents in the presence of a tin salt for room-temperature vulcanization. The effect of different fillers on the mechanical and thermal properties is also considered.

## EXPERIMENTAL

### Synthesis of Poly(dimethylsiloxane Diol)

Linear poly(dimethylsiloxane diol) was prepared<sup>10</sup> by dropwise addition of dimethyldichlorosilane to a saturated solution of sodium chloride in 1:2 ratio (by volume) at 0-5°C over a period of 2 hr. The reaction mixture was kept at

room temperature for about 20 hr, extracted with ether, and dried over anhydrous sodium sulfate. Intrinsic viscosity of poly(dimethylsiloxane diol) determined in toluene at  $(30 \pm 1)^\circ\text{C}$  using an Ubbelohde viscometer was found to be 0.18. The molecular weight distribution  $M_w/M_n$  was found to be 1.6 by gel permeation chromatography. Universal calibration curve was obtained by using standard polystyrene samples (Waters Associates).

### Preparation of Catalyst for Curing

The catalyst was prepared by mixing accurate amounts of tri- or tetrafunctional silane (methyltriethoxysilane, phenyltriethoxysilane, tetraethoxysilane, and methyltriacetoxysilane) and dibutyltin dilaurate in a 3:1 ratio, respectively.

### Formulation

The polymer was compounded with fillers of different particle sizes such as titanium dioxide ( $0.3 \mu\text{m}$ ), Cab-O-Sil ( $14 \text{ m } \mu\text{m}$ ), Dicalite White ( $2.4\text{--}2.8 \mu\text{m}$ ), and Dicalite PS ( $2.3\text{--}2.8 \mu\text{m}$ ) on a  $6 \times 2 \text{ in.}^2$  laboratory roll mill. Ten grams of the unfilled or filled polymer was weighed accurately and 2% catalyst was added to it. Blending was accomplished with a broad-blade spatula by steady mixing for 5 min and the mixture was poured into molds and cured at room temperature. The curing environment was room air over a period of 20 to 40 hr. Vacuum treatments were carried out before pouring to remove entrapped air.

### Mechanical Testing

All mechanical tests were made using an Instron mechanical tester on standard ASTM "dogbones." Ten samples were taken for each test. Load-elongation curves were obtained with the following settings on the Instron: gauge length, 2cm; cross-head speed, 10 cm/min; and chart speed, 10 cm/min on a full-scale load of 2 kg.

### Degree of Swelling

The degree of swelling of filled and unfilled silicone rubber was determined in different solvents at  $30^\circ\text{C}$ . Samples (approximately  $2 \times 2 \times 0.15 \text{ cm}^3$ ) were cut from the elastomers and weighed accurately. The sample was immersed in a large excess of solvent. The solvents were dioxane, acetone, toluene, carbon tetrachloride, *n*-heptane, and *n*-hexane. The rubber was removed after specific intervals of time; the surface solvent was blotted with filter paper and weighed in a stoppered bottle. Weight of the sample was recorded at 5, 10, 15, 30, and 45 sec after the removal of the sample from the solvent. The swollen weight was determined by linear extrapolation to zero time. The sample was air dried to constant weight. The above procedure was repeated until the equilibrium swollen state was reached. The amount of extractable polymer was determined at each interval. The % volume swell is determined by using the following equation:

$$\% \text{ volume swell} = \frac{\text{volume of swollen sample}}{\text{volume of dried sample}} \times 100$$

The volume fraction of rubber in the equilibrium swollen state was calculated which was related to crosslink density or the number-average molecular weight between crosslinks,  $M_c$ , by the Flory equation.<sup>11</sup>

### Effect of Saline Water

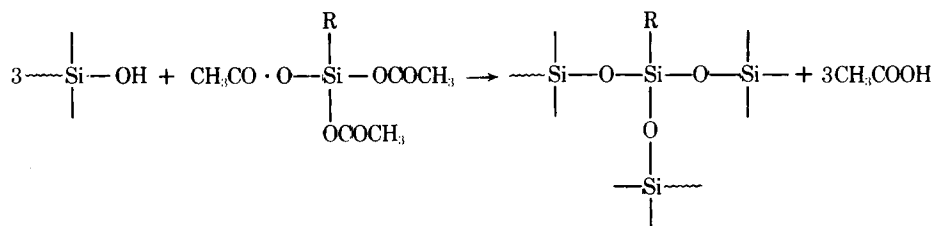
To evaluate the physiologic feasibility of silicone rubbers, a weighed sample (about 0.3 g) was immersed in saline water of 0.9% (w/v) concentration which is equivalent to the concentration of the body fluid (the samples were immersed for 22, 70, 166, and 670 hr at 30°C) and taken out and washed with distilled water. The samples were then wiped and weighed. The difference between the weight of a sample at a given time and the original weight was taken as the saline water uptake.

### Heat Aging

The samples were aged in the oven at 150, 200, and 250°C. At intervals the samples were removed and tested for weight loss.

## RESULTS AND DISCUSSION

The efficiency of various crosslinking agents as a function of setting time and the crosslink density is shown in Table I. A perusal of the data reveals the higher reactivity of methyltriacetoxysilane. Vulcanization takes place by hydrolytic cleavage of the acetoxy group from silicon atoms, i.e., a condensation of silanol and acetoxy group takes place with continuous displacement of the equilibrium by the evaporation of the acetic acid formed:



This is similar to the crosslinking phenomenon reported for single-component systems.<sup>5</sup> The alkoxy silanes are less efficient than acetoxy silanes, which may be related to the electronegativity of the functional groups<sup>12</sup>:

TABLE I  
Efficiency of Crosslinking Agents

Crosslinking agent	Setting time, hr	In toluene	
		$M_c$	$N \times 10^{-5}$ moles crosslinks/cm <sup>3</sup> polymer
Methyltriacetoxysilane	12	42032	2.47
Tetraethoxysilane	20	55443	1.87
Phenyltriethoxysilane	26	38482	2.70
Methyltriethoxysilane	38	39260	2.62

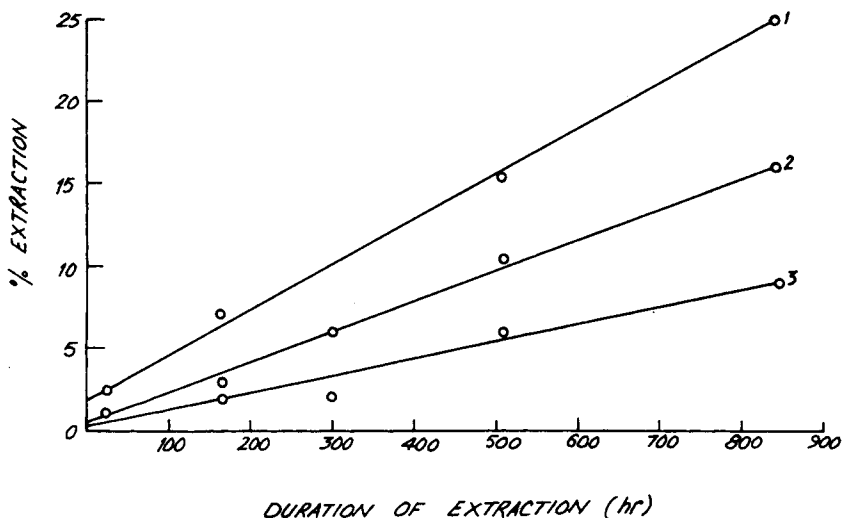
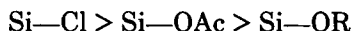
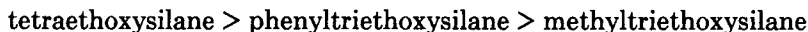


Fig. 1. Extraction of polymer from swollen samples during immersion in toluene. Unfilled silicone rubber vulcanized with (1) 1% curing mixture, (2) 2% curing mixture, and (3) 5% curing mixture.



Further, tetraethoxysilane has greater reactivity in terms of setting time than triethoxysilanes:



The higher reactivity of phenyltriethoxysilane as compared to methyltriethoxysilane may be related to the electron-withdrawing nature of the phenyl groups which makes the silicon more electropositive so as to favor nucleophilic substitution reaction. In room-temperature vulcanization, tin catalyst probably forms an active complex with the hydroxyl groups of the polymer which then reacts with the crosslinking agent as suggested by Mayhan et al.<sup>9</sup>

### Effect of Curing Mixture (Crosslinker + Catalyst) Concentration

The extraction of unfilled rubber swollen in toluene has been studied as a function of time (Fig. 1), which indicates that the amount of polymer extracted is dependent on the curing mixture concentration and consequently on the extent of crosslinking.

The amount of unextracted polymer also depends on the solubility parameter of the solvent which leads to variation in the amount of network expansion. This

TABLE II  
Extraction of Unfilled Silicone Elastomer

Solvent	Solubility parameter $\delta$ , ( $\text{cal}/\text{cm}^3$ ) <sup>1/2</sup>	Unextracted polymer at different intervals, %				
		24 hr	1 week	2 weeks	3 weeks	5 weeks
Acetone	9.1	96.1	94.6	43.5	90.0	90.0
Toluene	8.9	94.4	90.2	86.0	86.1	86.0
<i>n</i> -Heptane	7.4	91.0	82.3	73.1	73.0	73.0
<i>n</i> -Hexane	7.3	93.0	84.7	80.0	78.2	78.2

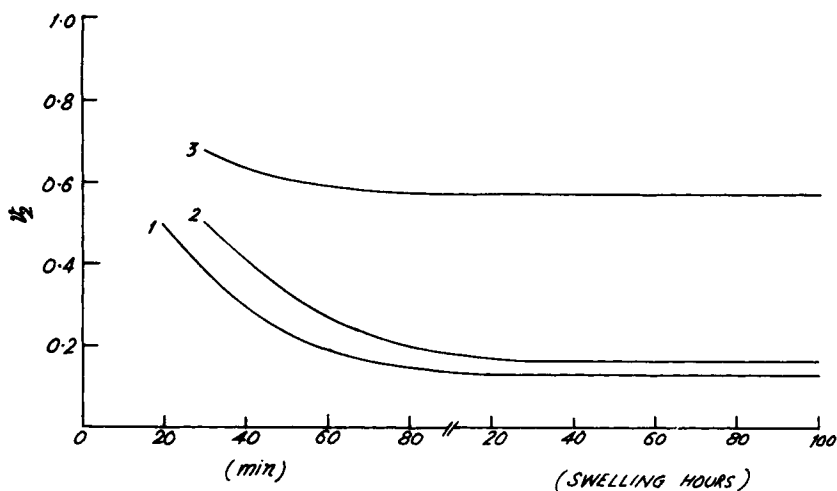


Fig. 2. Equilibrium swelling of vulcanized unfilled silicone elastomer in different solvents: (1) dioxane; (2) toluene; (3) *n*-hexane.

has been established from the extraction data (Table II) of unfilled elastomer in different solvents. In acetone, the rubber is only partly soluble, therefore, only 10% of the polymer could be extracted in approximately five weeks, whereas in *n*-heptane 27% of the polymer was extracted.

TABLE III  
Swelling of RTV Silicone Rubber (Unreinforced)

Swelling agent	cm <sup>3</sup> V <sub>1</sub> mole	δ, (cal/cm <sup>3</sup> ) <sup>1/2</sup>	V <sub>2</sub>	M <sub>c</sub> (1/2 - μ) <sup>a</sup>	Volume swell, %
Dioxane	117.831	10.0	0.6944	136.8	144
Acetone	73.511	9.9	0.5714	127.4	175
THF	81.633	9.1	0.2105	938.6	475
Toluene	106.125	8.9	0.1701	1790.3	588
CCl <sub>4</sub>	96.855	8.6	0.1562	1902.3	640
<i>n</i> -Heptane	146.263	7.4	0.1208	4527.1	828
<i>n</i> -Hexane	130.42	7.3	0.1259	3753.2	794

<sup>a</sup> μ = 0.465 in toluene, 0.38 in *n*-heptane, and 0.369 in *n*-hexane.

TABLE IV  
Swelling of PDMS Reinforced with 12.5 phr Dicalite White

Swelling agent	V <sub>1</sub> , cm <sup>3</sup> /mole	δ, (cal/cm <sup>3</sup> ) <sup>1/2</sup>	V <sub>2</sub>	Volume swell, %
Dioxane	117.831	10.0	0.7407	135
Acetone	73.511	9.9	0.5464	183
THF	81.633	9.1	0.1647	607
Toluene	106.125	8.9	0.1558	642
CCl <sub>4</sub>	96.855	8.6	0.1319	758
<i>n</i> -Heptane	146.263	7.4	0.1145	873
<i>n</i> Hexane	130.42	7.3	0.1188	842

TABLE V  
Swelling of PDMS Reinforced with 12.5 phr Dicalite PS

Swelling agent	$V_1$ , cm <sup>3</sup> /mole	$\delta$ , (cal/cm <sup>3</sup> ) <sup>1/2</sup>	$V_2$	Volume swell, %
Dioxane	117.831	10.0	0.6897	145
Acetone	73.511	9.9	0.5001	200
THF	81.633	9.1	0.1458	686
Toluene	106.125	8.9	0.1348	742
CCl <sub>4</sub>	96.855	8.6	0.1176	850
<i>n</i> -Heptane	146.263	7.4	0.1053	950
<i>n</i> -Hexane	130.42	7.3	0.1096	912

### Swelling Studies

The equilibrium volume fraction of polymer within the swollen network,  $v_2$ , shows a constant value after an initial decrease with time (Fig. 2). When the swollen gel is in equilibrium with the pure solvent, Flory's equation<sup>11</sup> is applicable for calculating the crosslink density:

$$Z = \frac{-(v_2^{1/3} - v_2/2)}{\ln(1 - v_2) + v_2 + \mu v_2^2} \quad (1)$$

where  $Z$  is ratio of the volume of a chain to the volume of a solvent molecule,  $\mu$  is the polymer-solvent interaction parameter, and  $v_2$  is the reciprocal of the equilibrium swelling volume ratio. If  $Z$  is replaced by  $M_c/\rho V_1$ , then eq. (1) may be represented as

$$M_c = \frac{-\rho V_1(v_2^{1/3} - v_2/2)}{\ln(1 - v_2) + v_2 + \mu v_2^2}$$

$$\ln(1 - v_2) + v_2 + \mu v_2^2 = NV_1(v_2^{1/3} - v_2/2)$$

where  $N$  = moles of crosslinks/cm<sup>3</sup> polymer. From the results (Tables III to V), it is evident that the higher the volume swell, the smaller will be the crosslink density in a given polymer-solvent pair.

Further, the volume swell percentage for unfilled vulcanized elastomer is small as compared to the elastomers reinforced with 12.5 phr Dicalite White and Dicalite PS. However, titanium dioxide-reinforced elastomer showed even lower volume swell percentage than the vulcanized unfilled sample. The volume swelling can be related directly to crosslink density (Table VI), though surface area, particle size, and chemical structure of the filler may influence the swelling

TABLE VI  
Effect of Crosslink Density on Mechanical Properties

Filler, phr	In <i>n</i> -Heptane			$N \times 10^{-5}$ moles crosslinks/cm <sup>3</sup> polymer	Tensile strength, kg/cm <sup>2</sup>	Elongation, %	Shore hardness
	Density of rubber	Volume swell, %	$M_c$				
None	1.04	828	27548	3.77	0.8	320	2
Dicalite White (12.5)	1.17	873	34584	3.38	8.0	180	38
Dicalite PS (12.5)	1.14	950	39928	2.85	6.0	190	33
Titanium dioxide (25)	1.09	620	21241	5.13	9.0	145	42

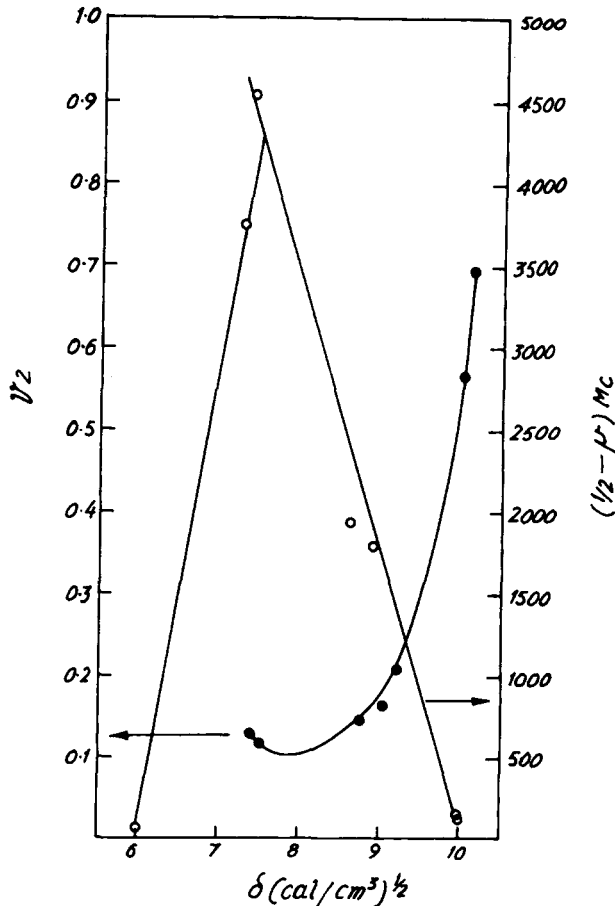


Fig. 3. Determination of solubility parameter of vulcanized unfilled silicone elastomer.

TABLE VII  
Reinforcing Fillers for Silicone Rubber

Filler	Type	Manufacturer	Surface area, $\text{m}^2/\text{g}$	Specific gravity	pH (4% in $\text{H}_2\text{O}$ )	Particle size, $\mu\text{m}$
Cab-O-Sil MS-7	fumed silica	Cabot Corporation	$200 \pm 25$	2.20	3.6-4.2	0.014
Dicalite PS	calcined diatomaceous silica	Dicalite Division, Grefco Inc.	2.5	2.25	6.0-8.0	2.3-2.8
Dicalite White	Flux calcined diatomaceous silica	Dicalite Division, Grefco Inc.	1.9	2.33	9.0-10.0	2.4-2.8
Titanox RA	titanium dioxide	Titanium Pigment Corp. N.Y.	—	4.2	—	0.3

behavior of these elastomers. It is worthwhile to mention that Flory's equation, though derived for nonpolar solvents, has been used to relate  $\nu_2$  with crosslink density in fluorosilicones when swollen in ethyl acetate<sup>13</sup> and for poly(diphenyl siloxane-*b*-dimethylsiloxane-*b*-diphenylsiloxane) copolymers.<sup>14</sup> In the present study, it was necessary to calculate  $M_c(1 - \mu)$  for determining the solubility

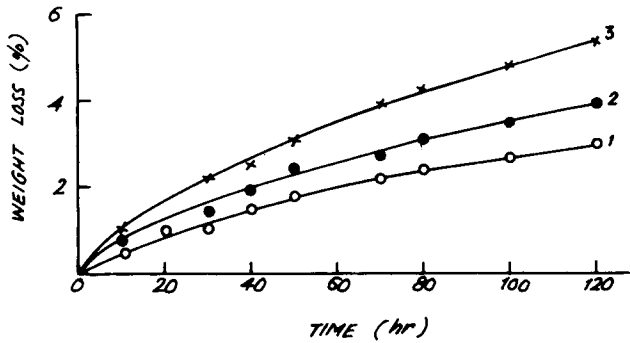


Fig. 4. Thermal aging of vulcanized unfilled silicone elastomer in air: (1) 150°C (2) 200°C; (3) 250°C.

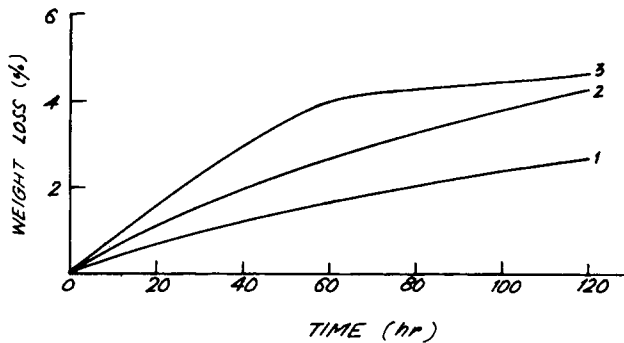


Fig. 5. Thermal aging of silicone elastomer reinforced with titanium dioxide (12.5 phr) in air: (1) 150°C; (2) 200°C; (3) 250°C.

TABLE VIII  
Mechanical Properties of RTV Silicones<sup>a</sup>

Reinforcing filler, phr	Tensile strength, kg/cm <sup>2</sup>	Elongation, %
Unfilled rubber	0.8	320
Cab-O-Sil MS-7 (12.5)	7.5	210
Dicalite White (12.5)	8.0	180
(25.0)	13.5	145
(50.0)	19.0	132
(100.0)	40.0	120
Dicalite PS (12.5)	6.0	190
(25.0)	9.0	155
Titanium dioxide (25.0)	9.0	145
(100.0)	28.0	130

<sup>a</sup> Curing mixture: methyltriethoxysilane plus dibutyltin dilaurate.

parameter of the unreinforced silicone rubber, but moles of crosslinks ( $N$ ) were calculated only from the swelling data obtained from *n*-heptane.

The solubility parameter of the unreinforced vulcanized silicone elastomer



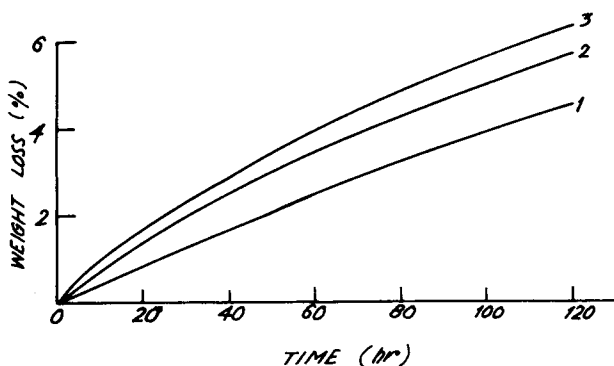


Fig. 6. Thermal aging of silicone elastomer reinforced with Dicalite PS (12.5 phr): (1) 150°C; (2) 200°C; (3) 250°C.

was found to be  $7.6 \text{ (cal/cm}^3\text{)}^{1/2}$  (Fig. 3). These values are comparable with those reported by Bueche<sup>15</sup> (7.7) and by Yerrick<sup>16</sup> (7.5).

#### Effect of Saline Water

The samples were immersed in 0.9% (w/v) saline water for about 22, 70, 166, and 670 hr at room temperature, and no change in the weight of the sample was observed, indicating no reaction with body fluid.

#### Mechanical Properties

The reinforcement of rubbers by various fillers depends on a number of factors, e.g., particle size, structure, and filler loading, which determine the extent of interaction with the silicone rubber. Silica fillers are the best reinforcing fillers for silicones as they are heat resistant and do not catalyze the decomposition of the polymer itself. The quality of filler used is an important factor in determining the processability of the compound and the character of the cured elastomer. The properties of the fillers used in this study are given in Table VII. The values of tensile strength and elongation for the unfilled and filled room-temperature vulcanized elastomers are given in Tables VI and VIII. Silicone rubber possesses very poor mechanical properties when unfilled. The tensile strength, however, increases with increase in filler content. The strength properties also seem to be dependent on the particle size and the surface area of the reinforced filler, for example, silicone rubber reinforced with 12.5 phr Dicalite PS showed a tensile strength of  $6 \text{ kg/cm}^2$  as compared to  $8 \text{ kg/cm}^2$  for the Dicalite White-reinforced elastomer. As Dicalite PS possesses a larger percentage of bigger particle size than Dicalite White, the interaction between silica filler and silicone rubber would be low.

The other factors which influence the tensile properties of reinforced elastomers are the chemical nature of the filler surface and the structure and porosity of the filler. In the case of Cab-O-Sil, the curing rate is quite high due to the accessible silanol groups available for crosslinking. This causes some crosslinking before applying or crepe hardening occurs. Therefore, proper mixing of Cab-O-Sil is not possible and high-strength material could not be produced.

### Effect of Thermal Aging of Silicone Elastomer

Network scission during heating of silicone elastomer in air would lead to (i) depolymerization or reversion to low molecular weight cyclic products; and (ii) hydrolytic scission at siloxane bonds in the main chain. The losses in weight observed on heating silicone vulcanizates (filled and unfilled) in air at 150, 200, and 250°C are shown in Figures 4 to 6. At all temperatures the rate of degradation is maximum in silicone elastomer reinforced with Dicalite PS, which may be attributed to the presence of base catalyst residues and pH of the filler (pH 6–8) which might accelerate the depolymerization. Moreover, from the swelling data it is evident that the crosslink density is also low in Dicalite PS.

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