

# Electric Conductivity of Silicone Elastomers Vulcanized by the Hydrosilation Reaction

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## Synopsis

Electrical conductance and hardness of silicone elastomers, prepared by the vulcanization reaction of hydrosilyl groups with vinyl groups in the presence of platinum catalyst, were measured. It is shown that the electric conductivity of the elastomers decreases as hardness increases and as the temperature decreases. An empirical equation is derived expressing electric conductivity  $\sigma$  as a function of hardness  $H$  and absolute temperature  $T$ ,  $\log \sigma = -0.03H - 3200/T - 3$ , where  $\sigma$  is  $S/m$  and  $H$  is Shore A, over the temperature range of 100–150°C.

## INTRODUCTION

While mechanisms of electrical conductance in insulating polymers have been extensively investigated<sup>1-3</sup> and discussed using experimental results on temperature dependencies of electric conductivity, only a few activation energies for the electric conductivity for silicone elastomers have been reported.<sup>4</sup>

The effects of heat treatment on electrical properties of silicone rubbers vulcanized by the condensation reaction had been investigated in our previous papers.<sup>5,6</sup> The present paper continues these studies, elucidating the factors which determine the electric conductivity of silicone elastomers vulcanized by the addition reaction of the hydrosilyl group with vinyl groups. The influences of activation energy and hardness will be discussed here.

## EXPERIMENTAL

**Materials.** The unfilled polydimethylsiloxanes used in this investigation were commercially available two-component types (Table I). The viscosities, before curing, listed for them shown serve as indicators of their molecular weights. The liquid silicones were prepared from prepolymer containing vinyl groups ( $\equiv\text{Si}-\text{CH}=\text{CH}_2$ ), crosslinker containing hydrosilyl groups ( $\equiv\text{S}-\text{H}$ ) and platinum catalyst.<sup>7,8</sup> Impurities present, such as sodium ion, were shown to be less than 1 ppm by atomic absorption analysis.

A mixture of liquid silicone was spread on an aluminum board having a mirror finish. The board was placed on a horizontal plate of iron in an oven, and cured under appropriate conditions which are shown in Table I.

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TABLE I  
 Compositions of Silicone Gels and Rubbers

Type	No.	Viscosity 25°C (Pa·s)		Curing condition (°C/h)	Commercial name <sup>a</sup>	
		A	B			
Gel	G1	50	5	100/1+150/16	KE104GEL	*1
	G2	90	25	25/16+100/4	SH1851	*2
	G3	55	20	25/16+100/4	TSE3031	*3
Rubber	R4	65	5	100/1+150/16	KE103	*1
	R5	230	40	100/1+150/16	KE106	*1
	R6	130	34	100/1+150/16	52-003	*1
	R7	300	30	100/1+150/16	TSE3032	*3
	R8	1500	37	150/2+200/16	R6014	*4
	R9	550	5	150/2+200/16	R6103	*4

<sup>a</sup> 1: Shin-etsu Kagaku; \*2: Tore Silicone; \*3: Toshiba Silicone; \*4: Dow Corning. Weight ratio A/B = 10/1.

**Measurements.** Electrical conductance of specimens (1 mm thick) was measured at 30 V in the temperature range from 100°C to 150°C, after charging of direct current for 1 h to saturate the current. Main and guard-ring electrodes made of aluminum, with diameters of 5 and 5.2 cm, respectively, were used. The electrode surfaces were mirror finished to ensure close adherence.

The silicone boards (1 cm thick) were used to measure their hardness at various temperatures.

## RESULTS AND DISCUSSION

### Activation Energy and Mechanism

Figure 1 shows the temperature dependence of the electric conductivities for various silicone gels and rubbers. The electric conductivities of the rubber specimens R4–R9 ranged from  $10^{-14}$  to  $10^{-12}$  S/m at 100°C, which are lower than those of silicone gel specimens G1–G3. The former values also seem to be lower than those for other insulating polymer materials such as amorphous polyethylene terephthalate ( $10^{-12}$  S/m at 100°C).<sup>9</sup>

Activation energies for electric conductivity were obtained for silicone rubbers and gels from Arrhenius plots and ranged from 42 to 60 kJ/mol. Our activation energies are remarkably low compared to those of such well-known insulating polymers as polyester and epoxide resin which have been reported to be 142 kJ/mol at 30–90°C<sup>10</sup> and 214 kJ/mol at 100–130°C,<sup>1</sup> respectively.

Conduction mechanisms for various insulators have been discussed on the basis of activation energy values. For example, cellulose acetate doped with alkali-halide was found to have an activation energy of 586 kJ/mol, which corresponds to the dissociation energy of alkali-halide by the absorbed moisture.<sup>11</sup> However, this value is so high that it is impossible to compare it with our activation energies. On the other hand, the carriers

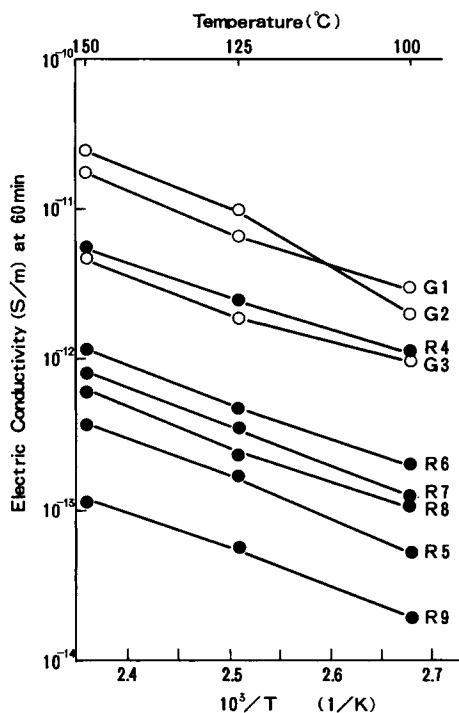


Fig. 1. Temperature dependence of electric conductivity for various silicones (G:gels; R:rubbers).

in poly(vinyl fluoride) have been proposed to be halo ions such as fluoro ions, where activation energy is 92 kJ/mol.<sup>2</sup> The carriers in the silicone elastomer vulcanized by the hydrosilation reaction in these experiments would not be expected to be halide ions such as chloro ions contained in the chloroplatinic acid ( $\text{H}_2\text{PtCl}_6$ ) used as the catalyst,<sup>8</sup> since our value is smaller than that for halide ions such as fluoro ions and the concentration is very low.

Absorption current is induced by oriented dipole moments or space charge electrons<sup>12</sup> and is quickly saturated with increasing temperature, charge time, and electric field.<sup>9,13</sup> However, the conduction in silicone elastomer should not be due to orientation of the dipole moment of residual unreacted groups or to space charge electrons, since the charging was carried out at high temperatures for a long time. Therefore, it would be reasonable to conclude that the conduction is not due to chloride ion carriers or dipoles.

Heats of decomposition have been given as 32<sup>14</sup> or 57 kJ/mol<sup>15</sup> for monosilane and as 77 kJ/mol<sup>14</sup> for disilane. These decomposition energies are comparable to our activation energies. On the other hand, it has been proposed that protons dissociated from the residual carboxylic acid groups which remain as unreacted groups can diffuse as charge carriers through the poly(ethylene terephthalate)<sup>1</sup> and the dry polyimide.<sup>3</sup> Taking this into account, we consider that the rate-determining process in the electric conduction of polydimethylsiloxane is decomposition of hydrosilyl groups to release protons. Accordingly, protons seem to be the charge carriers in our study.

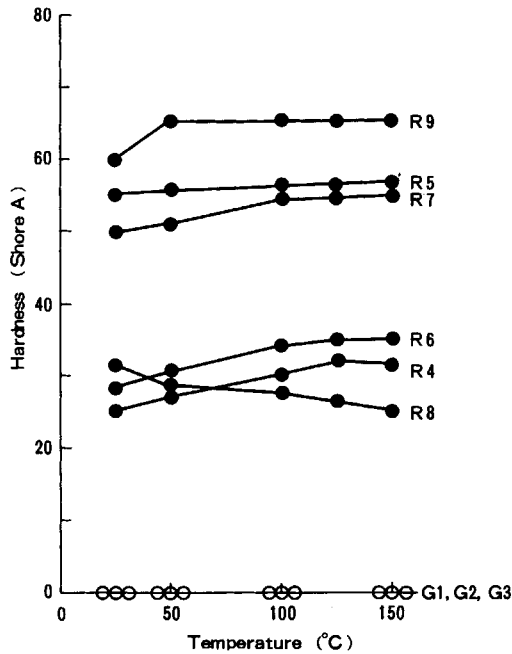


Fig. 2. Temperature dependence of hardness for various silicones (G:gels; R:rubbers).

### Temperature Dependence of Hardness

The hardness of silicone rubbers shows a temperature dependency, increasing with increasing temperature, except for R8, as shown in Figure 2. The hardness of silicone gels was almost 0 in the same temperature range. It has been reported<sup>16,17</sup> that above  $T_g$  the hardness of polyvinyl formal and polyester resins become higher with increasing crosslinking densities. Elastomer hardness thus reflects the crosslinking densities of polymers. It has also been reported that the tensile strength of silicone rubbers increases with increasing temperature.<sup>18</sup> The results in Figure 2 suggest that the crosslinking densities differ depending on the silicone rubber specimens; the higher the hardness, the higher the crosslinking density.

### Factors Influencing Electrical Conductivity

The relationship between the hardness and the electric conductivity of silicone gels and rubbers at 100°C is plotted in Figure 3. Electric conductivity decreases with increasing hardness of the elastomer.

Electric conductivity should be a function of charge concentration and mobility. Even though the nature of the carrier has not been clarified at present, however, if it is assumed that the concentration of charge carriers in the silicone rubbers and gels used here is almost the same, the results in Figure 3 suggest that mobilities of the charge carriers are restrained by the hardness of the polymer matrix, that is, by the crosslinking density of the matrix. The data plotted in this figure could be fitted to

$$\log \sigma = A^*H + B \quad (1)$$

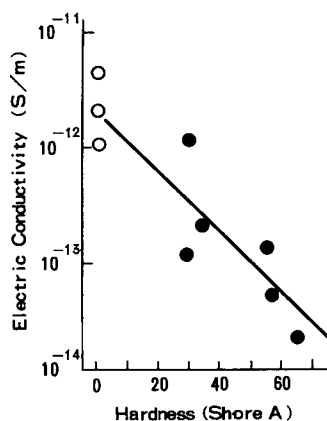


Fig. 3. Relationship between the electric conductivity and the hardness of silicones [(●) R:rubbers] and [(○) G:gels].  $\log \sigma = -0.03H - 11.6$ ;  $c = -0.90$ . 100°C; 1 h; 30 V/mm.

where  $\sigma$  is S/m,  $H$  is Shore A, and  $A$  and  $B$  are constants determined by the least-squares method (Table II).

The relationship between the hardness and the electric conductivity appears valid, even though the correlation coefficient at 100°C is 0.90. Values of  $A$  vary slightly, with an average value of  $-0.03 \pm 0.004$ . On the other hand, the value of  $B$  increases with increasing temperature.

Electric conductivity expressed by eq. (1) can be rewritten as eq. (2), which includes the reciprocal of the absolute temperature:

$$\log \sigma = -0.03H - 3200/T - 3 \quad (2)$$

Activation energy is calculated to be 62 kJ/mol using the reciprocal of the absolute temperature. This value is almost the same as that obtained from an Arrhenius plot. Thus electric conductivity of silicone elastomers can be expressed as a function of hardness and temperature using eq. (2) over the range of 100–150°C.

### CONCLUSION

The electric conductivity of silicone elastomers vulcanized by the hydrosilation reaction depend not only on temperature, but also on the elastomer hardness. An empirical equation for electric conductivity was obtained as a function of these two parameters over the temperature range of 100–150°C. Activation energies of electrical conductivity are in the range of 42–60 kJ/mol, which are much lower than those for other typical insulating polymer materials.

TABLE II  
Values for  $A$  and  $B$  of Eq. (1) and the Correlation Coefficient  $C$

Temp (°C)	$A$	$B$	$C$
100	-0.030	-11.6	-0.90
125	-0.026	-11.4	-0.86
150	-0.034	-10.6	-0.90

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