

Factors Causing Variations in Electrical Properties and Hardness of Silicone Rubbers

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Synopsis

Influence of preparation conditions on the electrical conductivity, dissipation factor, and hardness of silicone rubber vulcanized by the condensation reaction using dibutyltin dilaurate as catalyst was studied. Thickness of rubber specimens and amounts of catalyst added were varied. Electrical properties were measured at 20–200°C for rubber specimens heat-treated at 200°C for 10 h under various conditions, for example, heat treated in air, but in a sealed state in order to inhibit volatilizations of the catalyst and vaporization of by-products, or heat treated in a dry nitrogen atmosphere, in order to avoid oxidation and hydrolysis of the catalyst. Furthermore, the catalysts and byproducts were volatilized in air from both surfaces of the specimen in order to accelerate volatilization. Degradation of silicon rubber with heat treatment was elucidated by hardness measurements and hardness dependence of the electrical conductivity of the specimens was analyzed.

INTRODUCTION

Electrical and electronic devices require materials showing excellent insulation properties. As such, silicone elastomers vulcanized by condensation and hydrosilation reactions have been widely used as insulation and passivation layers for semiconductor devices, including diodes, transistors, and thyristors, and as protection layers against discharges in high voltage devices. It is necessary to ensure that device operation is not adversely affected at high temperatures by the silicone elastomers when used as insulation and protection layers. Therefore, elucidation of insulation properties at high temperatures is particularly important for stable device operation. Electrical properties of silicone elastomers have been studied by many investigators.¹⁻³ Since excellent insulation properties are needed for the polymers used in the various devices, a systematic development and improvement of materials are essential.

The authors have been studying factors causing variations in the electrical properties of silicone elastomers and have found that electrical conductivities of silicone elastomer vulcanized by the hydrosilation reaction can be expressed as a function of hardness.⁴ They have also reported that variations in electrical properties are induced by residue of hydrolyzed catalyst used during vulcanization⁵ and that the insulation properties are

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improved by heat treatment in a 100% oxygen atmosphere.⁶ However, this treatment is not practical for electrical and electronic assemblies constructed with easily oxidized electrodes, such as Al, Ag, Cu, and Pb-Sn, etc.

This paper continues these studies on electrical properties, elucidating the influence of the thickness, amount of added catalyst, and heat treatment conditions under various atmospheres and flow rates. Factors causing variations in the electrical properties and hardness are clarified here, and the relationship between electrical conductivity and hardness is discussed by comparing the condensation type silicone rubbers with hydrosilation ones.⁴

EXPERIMENTAL

Preparations

The liquid silicone is composed of ethoxysilane as crosslinking agent, α , ω -dihydroxypolydimethylsiloxane as prepolymer and calcium carbonate powder as mechanical reinforced agent and filler.^{5,6} A given amount (1.5–12 $\mu\text{mol/g}$) of dibutyltin dilaurate as catalyst was added to the liquid silicone. The mixture was then stirred and spread onto a polytetrafluoroethylene board at a desired thickness by using spacers of various heights (1–3 mm). The layer was vulcanized at 25°C for 4 h under 100% relative humidity.

Heat Treatment

All rubber specimens were heated at 200°C for 10 h in an oven (60 \times 60 \times 60 cm). Some specimens were heated in a sealed state, others were heated under air, and a third group was heated in an open state. These arrangements are shown schematically in Figures 1(A), (B), (C), respectively. A few other specimens were heated in dry nitrogen at a given flow rate (0.5–1.5 cm/s) under the semiopen state.

Measurements

Dissipation factors and electrical conductivities were measured in air at 50 Hz and 1 kV after a direct current charge of 1 min duration, respectively.^{5,6} Hardness of specimens formed by placing rubber sheets on top of each other to give a 1 cm thickness was measured at 25°C.

RESULTS AND DISCUSSION

Influence of Thickness

Figure 2 shows the effects of specimen thickness and amount of catalyst on the electrical properties for silicone rubbers heat treated in the semiopen state. Electrical conductivity and dissipation factor both increase with increasing thickness of rubber specimens at a given amount of catalyst. This tendency becomes more remarkable with larger amounts of catalyst. On the other hand, electrical conductivity and dissipation factor both become smaller with decreasing amounts of catalyst at a given thickness.

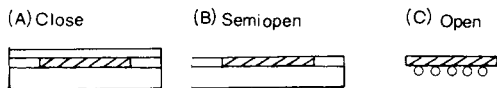


Fig. 1. Cross-section views of various heat treatment conditions for silicone rubber after vulcanization: (A) closed with polytetrafluoroethylene; (B) semiopen on polytetrafluoroethylene board; (C) open on a stainless-steel network.

Generally speaking, the vulcanization reaction should be accelerated by increasing the amount of catalyst. However, Figure 2 shows that acceleration of vulcanization is not the main factor which determines the excellent insulation properties of silicone rubber in these experiments. From a practical viewpoint, preparation of a thicker sheet should require smaller catalyst content while still obtaining excellent insulation properties.

In previous papers,^{4,6} we reported that chemical changes due to hydrolysis and oxidation take place in the catalyst itself resulting in changes of electrical properties. However, attention was not paid to physical effects such as volatilization of catalyst. If the volatilization of catalyst has any significant effect, it would be confirmed by analysis of residual tin content in the rubber specimen. Residual content of the catalyst was measured by colorimetric analysis of tin content. About half the original catalyst content remained and was detected in a specimen. Therefore, about half the amount was volatilized during the heat treatment.

Effect of Heat Treatment Conditions

Figure 3 shows the heat treatment effects on the electrical properties for the samples in which catalyst amount was varied. Both electrical conductivity and dissipation factor vary with heat treatment condition, and vol-

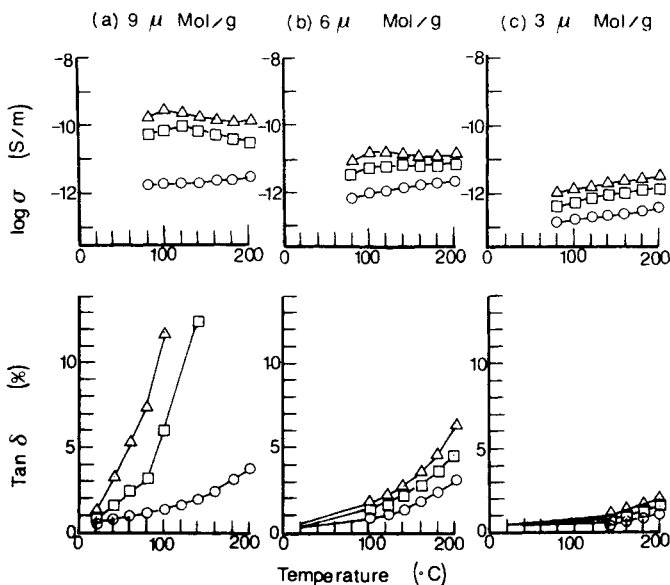


Fig. 2. Temperature dependence of electrical conductivity, σ , and dissipation factors, $\tan \delta$, for silicone rubbers with various thicknesses and amounts of added catalyst. Catalyst amounts ($\mu\text{mol/g}$): (a) 9; (b) 6; (c) 3; thickness (mm): (i) \circ 1; (ii) \square 2; (iii) \triangle 3 mm; condition in air : semiopen.

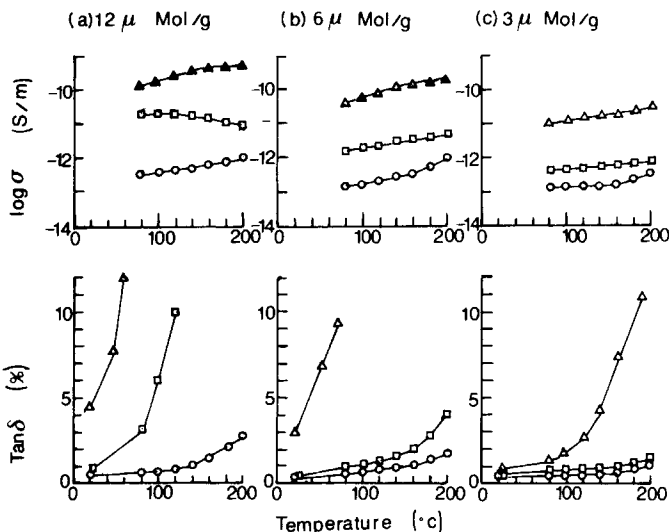


Fig. 3. Temperature dependence of electrical conductivity, σ , and dissipation factor, $\tan \delta$, for silicone rubber with various heat treatment conditions in air. Catalyst amounts ($\mu\text{mol/g}$): (a) 12; (b) 6; (c) 3; conditions in air: (A) (Δ) closed; (B) (\square) semiopen; (C) (\circ) open; thickness 1 mm.

atilization of catalyst seems to be inhibited under the closed condition and accelerated under the open one. Values of conductivity and dissipation factor become smaller in the following order, closed, semiopen, and open, at a given catalyst content [compare Figs. 3(A)–(C)], and their values decrease with decreasing catalyst content for a given condition.

Electrical conductivity increases with increasing temperature, except for some temperature dependences of that in Figures 2(a) and 3(b). Phenomenon giving exceptional temperature dependence might be induced by volatilization and/or oxidation, etc., during measurements in air. Heat treatment under an open condition provides a rubber sheet having excellent insulation properties which result from volatilization of the catalyst from both surfaces of the specimens. This phenomenon is observed more clearly when the catalyst content becomes larger. However, when the catalyst content becomes smaller as shown in Figure 4(A), even a closed condition can provide a rubber specimen having lower electrical conductivity and a smaller dissipation factor.

There is another method to decrease residual catalyst. Volatilization of the catalyst would be accelerated by ventilation during heat treatment. Thus rubber specimens were heated in an oven supplied with flowing dry nitrogen in order to avoid oxidation and hydrolysis of the catalyst and to allow elucidation of the volatilization effect. Values of the electrical conductivity and dissipation factor become smaller with increasing flow rate. This tendency becomes more remarkable with increasing catalyst amount as shown in Figure 5. It is confirmed that decreasing the amount of catalyst and accelerating its volatilization are required in order to obtain rubber sheets with excellent insulation properties.

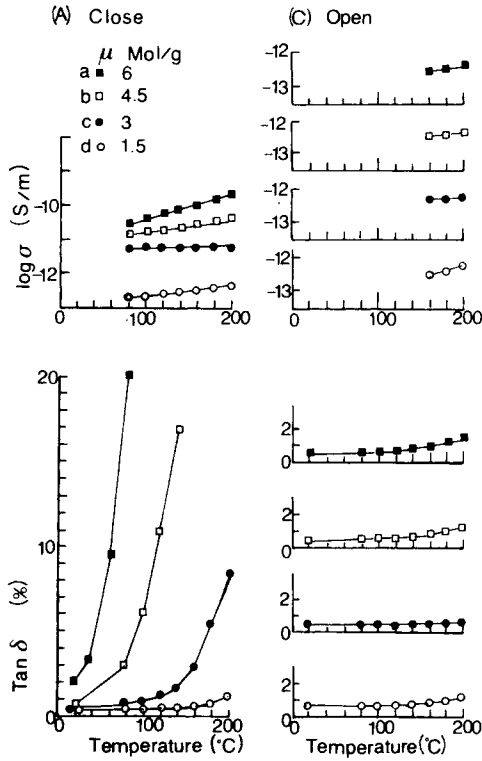


Fig. 4. Effects of decreasing amounts of added catalyst on electrical conductivity, σ , and dissipation factor, $\tan \delta$, with various heat treatment conditions in air. Conditions: (A) closed; (C) open; catalyst amounts ($\mu\text{mol/g}$): (a) (■) 6; (b) (□) 4.5; (c) (●) 3; (d) (○) 1.5; thickness: 1 mm.

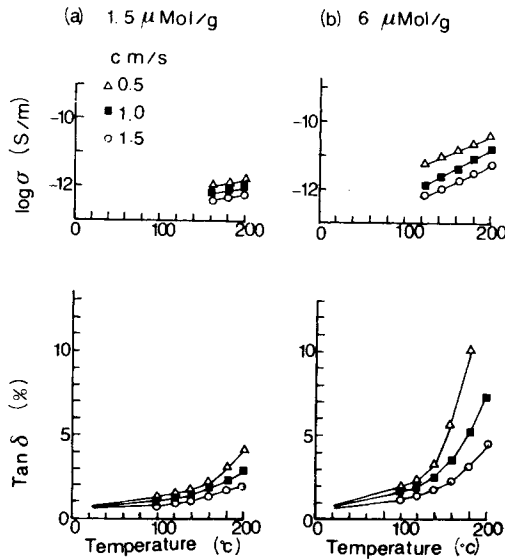
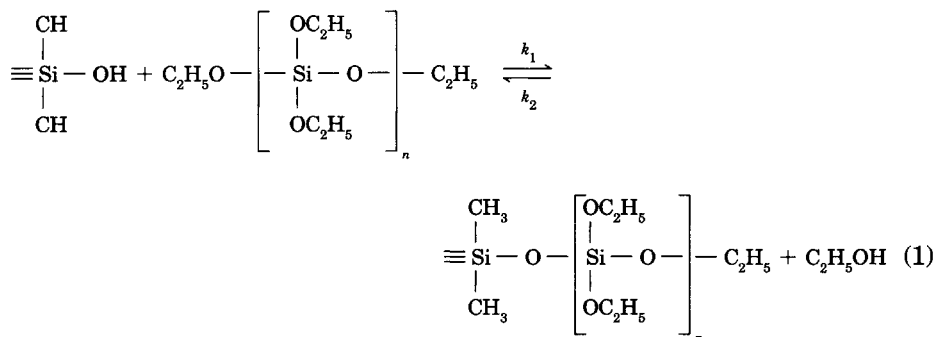


Fig. 5. Effects of dry nitrogen flow rate on the electrical conductivity, σ , and dissipation factor, $\tan \delta$. Catalyst amounts ($\mu\text{mol/g}$): (a) 1.5; (b) 6; flow rate (cm/s): (Δ) 0.5; (■) 1.0; (○) 1.5; condition: semiopen; thickness: 1 mm.

Influence of Hardness

It is generally thought that values of electrical conductivity and dissipation factor becomes smaller with increasing crosslinking density at a given concentration of charge carrier. This tendency has been found in silicone elastomer vulcanized by the hydrosilation reaction, that is, electrical conductivity decreases with increasing hardness.⁴ Therefore, hardness of the silicone elastomer is an important factor affecting electrical properties.

Silicone rubber specimens vulcanized at 25°C for 4 h indicate hardness values over 42 Shore A. Hardness of a completely vulcanized silicone specimen is 45 Shore A.⁶ It is expected that cross-linking reaction is proceeded by heat treatment, and the hardness value would become higher. However, the value of some samples decreased on heat treatment. The extent of the decrease varies with preparation and heat treatment conditions. Hardness decreases with increasing thickness at a given catalyst content, as shown in Figure 6. This tendency becomes larger with increasing amounts of added catalyst. Hardness values decrease also with heat treatment conditions in the following order, open, semi-open, and closed, at a given catalyst content, as shown in Figure 7. This order corresponds to that for degradation of insulation properties. Pyrolysis or decomposition takes place during the heat treatment resulting in a decrease in the rubber hardness when the thickness of the rubber and catalyst amount become larger and the volatilization area of the specimens becomes smaller. This is because the volatilization of the catalyst and byproducts would become more difficult for thicker specimens and smaller exposed areas during heat treatment. Since the degree of degradation increases with increasing inhibition of volatilization, the condensation reaction of hydroxy groups with ethoxy groups would be thought equilibrium one. The reaction is shown in eq. (1)



The equilibrium coefficient would be varied by the temperature and vaporization of the byproducts, etc. When the alcohol byproduct vaporizes and the catalyst volatiles from the specimen during heat treatment, the reaction with rate k_1 , that is, polymerization would progress. Therefore, dibutyltin dilaurate would act as a polymerization catalyst, when volatilization is accelerated. However, when vaporization is inhibited, the reaction with rate k_2 , i.e., decomposition, would progress. Therefore, dibutyltin dilaurate would act as a depolymerization catalyst when vaporization of byproducts

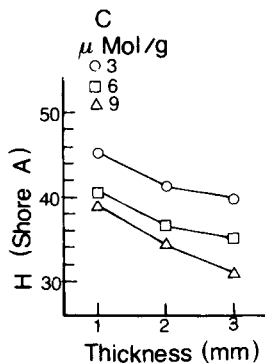


Fig. 6. Effect of thickness on hardness of silicone rubbers with various catalyst amounts ($\mu\text{mol/g}$): (○) 3; (□) 6; (△) 9. Preparations are the same as Figure 2.

is more difficult from thicker specimens and smaller exposed area during heat treatment. Depolymerization would be accelerated by increasing the catalyst content. Vaporization of byproducts and volatilization of the catalyst should be required to retard the degradation, since dibutyltin dilaurate may function as a depolymerization catalyst during heat treatment.

Linear relationships are also observed between the hardness values and electrical conductivity for the rubber specimens vulcanized by the condensation reaction in these experiments, as shown in Figure 8. The correlation coefficient is 0.92. The electrical conductivity at 150°C can be expressed as a function of hardness (H) by using eq. (2).

$$\log \sigma = -2.25 - 0.25H, \quad 30 < H < 45 \quad (2)$$

Equation (3) has been reported in a previous paper⁴ expressing the relationship between the hardness and electrical conductivities for rubber specimens vulcanized by the hydrosilation reaction:

$$\log \sigma = -10.6 - 0.03H, \quad 0 < H < 60 \quad (3)$$

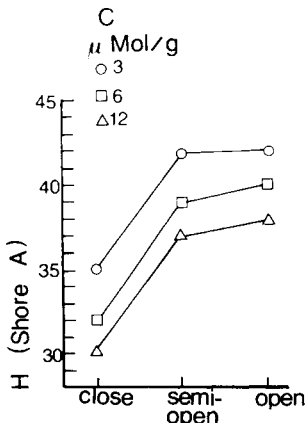


Fig. 7. Effect of heat treatment methods on hardness of silicone rubbers with various catalyst amounts ($\mu\text{mol/g}$): (○) 3; (□) 6; (△) 12. Preparations are the same as Figure 3.

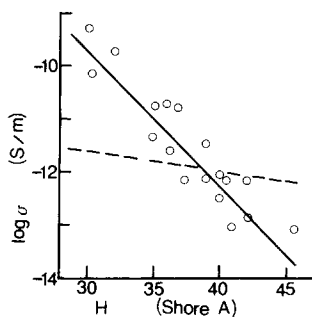


Fig. 8. Hardness dependence of electrical conductivity at 150°C; (a) (-O-) condensation reaction; (b) (- - -) hydrosilation reaction.⁴

Dependence of the electrical conductivity for the condensation reaction is larger than that for the hydrosilation one. This difference can be interpreted as occurring by two factors. Since the electrical conductivity increases with increasing amount of catalyst as shown in Figures 2 and 3, it is thought that one species of the carrier is a catalyst in the silicone elastomer vulcanized by the condensation reaction. If it is assumed that the charge carriers are also catalysts in the hydrosilation type rubber, the carrier would be a platinum compound.^{7,8} For the condensation reaction, 1–10 $\mu\text{mol/g}$ of catalyst are needed, while the catalyst amount in the hydrosilation type rubber is enough, and only 5–50 nmol/g .⁹ The latter values are much smaller than the former. Based on this assumption, one factor influencing the dependence of the electrical conductivity of silicone rubber vulcanized by the condensation reaction is catalyst content. Another factor relates to depolymerization. Mesh size would become wider due to cutting of the network in the polymer during heat treatment of thicker specimens, larger catalyst amounts, and smaller vaporization area, etc. Therefore, low molecular fragment would be produced. It is reasonable that charge carriers such as low molecular fragment can migrate easily in the polymer.

Appropriate conditions such as smaller amounts of added catalyst, and acceleration of volatilization and vaporization should be preferred in order to prepare condensation type silicone rubbers with excellent insulation properties when thicker specimens are used in closed systems at high temperatures.

CONCLUSION

The electrical conductivity, dissipation factor, and hardness of rubber specimens vulcanized by the condensation reaction using dibutyltin dilaurate as catalyst varied with their preparation conditions such as thickness, amount of added catalyst, and heat treatment after vulcanization at room temperature. Values of the conductivity and dissipation factor became larger with increasing thickness, catalyst amount, and by inhibiting vaporization of byproducts and volatilization of catalyst from the rubber specimen during heat treatment, but the hardness value became smaller. Residual catalyst acted as a decomposition catalyst resulting in the deterioration of the electrical properties. Low electrical conductivity and small dissipation factor were obtained by volatilization of catalyst and byproducts.

The electrical conductivity of silicone rubber vulcanized by the condensation reaction could also be expressed as a function of the hardness, just as the hydrosilation reaction could, but the actual dependence differed for the two.

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