

Polymerization of Epoxide with Aluminum Complex/ Silanol Catalyst. VII. Thermal and Electrical Properties of Epoxy Resin Cured with the New Catalyst

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Synopsis

Curing catalyst for epoxy resins was newly found. The catalyst consists of aluminum complex and silanol. Lack of one component of the pair does not cure epoxy resins. The epoxy resins cured with the catalyst are characterized by excellent electrical properties, especially at high temperature, due to the absence of strong acid species in the cured epoxy resin matrix. Heat-resistant property of the resin was also excellent. These properties were compared with those of epoxy resin cured with commonly used BF_3 complex.

INTRODUCTION

Epoxy resins have been utilized as insulating materials, coating materials, adhesives, and laminating materials in many fields. They are preferred for electrical properties, mechanical properties and the cost.¹ In the electrical industry, a number of epoxy resins have also been used as the materials for insulation of coils in generator and motor, molding compound for semiconductor encapsulation, the materials for the laminates for circuit plates. Excellent insulating properties, high reliability, and low cost have been required for the materials used for these purposes. There is a recent trend for many electrical appliances to be midget type. The temperature of the insulation materials rises; therefore, the insulation properties and heat-resistant properties must be improved, especially in the temperature range from 150°C to 220°C.

Epoxy resin monomer used has more than two epoxy groups for curing. The monomer forms 3-dimensional networks in the presence of catalyst. The catalyst used is then buried in the matrix of the network. Therefore, the following properties will be influenced by the catalyst residue: (1) insulation properties; (2) collosion properties on metal; (3) color change by aging at higher temperature; (4) heat-resistant properties, where the heat-resistant properties mean weight loss of the cured resin when it was aged at high temperature. The catalyst for ring-opening polymerization also degrades the polymer chain at that temperature. As shown above, the properties of epoxy resins cured can be improved by use of appropriate catalyst or by modification of the catalyst.

The following are the curing catalysts which have been commonly used for homopolymerization of epoxy resin monomers²: (1) tertiary amines (containing

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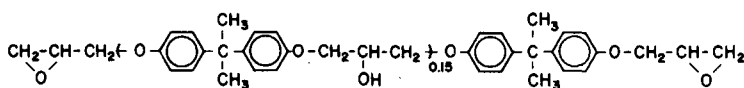
imidazole and guanidine); (2) BF_3 -amine complex (e.g., BF_3 -monoethyl amine and BF_3 -piperidine); (3) ammonium complex ($\text{C}_6\text{H}_5\text{NH}_3^+\cdot\text{AsF}_6^-$ and $\text{C}_6\text{H}_5\text{NH}_3^+\cdot\text{PF}_6^-$). The dissipation factor of the epoxy resin cured with these catalysts increased rapidly at the temperature over 150°C .

The following points were important for the development of new catalysts: (1) stability in air and toward moisture; (2) freedom from ionic species, e.g., halogen anion, metal cation, H^+ ; (3) high activity for epoxide polymerization. A new catalyst system was found from this point of view.³ The catalyst consists of aluminum complex and silanol compound. The epoxy resin cured with the present catalyst had excellent electrical properties. Since epoxides polymerize in terms of ionic mechanism, the absence of any appreciable ionic species after polymerization is intriguing. In the present catalyst, SiOH as ionic species is considered to disappear by self-condensation and the addition to epoxide. In this paper, the electrical properties and heat-resistant properties of the epoxy resin cured with the present catalyst were compared with that with BF_3 -complex. The dependence of the electrical properties on the structure of the catalyst was also reported.

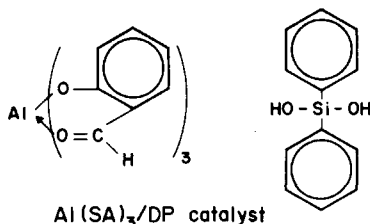
EXPERIMENTAL

Materials: Tris(acetylacetonato)aluminum, tris(ethylacetoacetato)aluminum, and tris(salicylaldehydato)aluminum were synthesized from aluminum isopropoxide and acetylacetone or ethylacetoacetate or salicylaldehyde.³ Aluminum complexes of these materials were purified by means of recrystallization or distillation. Triphenylsilanol and diphenylsilanediol were synthesized by means of hydrolysis of triphenylchlorosilane and diphenylsilanediol, and recrystallized from toluene and petroleum ether.³ Polymeric silanol (SH6018, Toray Silicone) and BF_3 -monoethylamine were purchased commercially. Bisphenol A type epoxide [Epikote 828, (Fig. 1), Shell Chemical Co.] was used as epoxy resin monomer.

Curing: The epoxy resin monomer containing the catalyst was poured into



Bisphenol A type epoxy resin



$\text{Al}(\text{SA})_3/\text{DP}$ catalyst

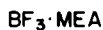


Fig. 1. Structure of epoxy resin and catalyst.

1-mm width opening between two glass plates which were covered with cellophane, and was cured at 150°C for 15 h, and then the cellophane on the cured resin was peeled off in water.

The measurement of thermal depolarization current was performed in the following manner. The curing conditions are summarized in Figure 4. An electrode was made of Ag and evaporated on the cured epoxy resin plate. Diameter of the electrode is 1 cm. A sample was polarized with electric field (E_p) at 150°C for 30 min and subsequently cooled rapidly to room temperature before the field was removed. After short-circuiting the electrodes, the sample was heated at a constant rate of 3°C/min, and the current was measured, using an Electret Thermal Analyzer No. 650 (Toyo Seiki Seisaku-sho, Ltd.).

Volume resistivity was measured as follows. An electrode was made of Au and was evaporated on the cured epoxy resin plate, as shown in Scheme 1. The sample was heated at 0.75°C/min. The impressed voltage was 500 V (Model 4329, Yokokawa-Hewlett Packard).

Dielectric constant and electrical dissipation factor were measured by use of Schering Bridge Type 2759 (Yokokawa Electric Works, Ltd.) at 50 Hz, 500 V. Electrode structure are same as that of volume resistivity measurement.

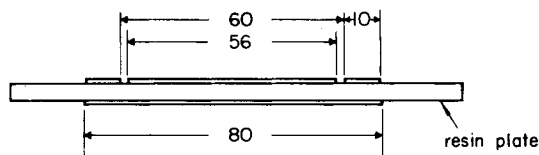
Measurement of breakdown voltage was performed as follows. The sample was placed between stock (6ϕ) and plate in silicone oil. Impressed voltage was increased at 1 kV/s at AC 50 Hz. The sample thickness is 1 cm.

Modulus of elasticity was measured by means of torsional braid analysis (RD 10 type, Resca). The size of the sample is as follows: 1 mm \times 10 mm \times 80 mm.

RESULTS AND DISCUSSION

Difference in Electrical Properties between Epoxy Resin Cured with BF_3 Complex Catalyst and That Cured with Tris(salicylaldehydato) Aluminum/Diphenylsilanediol Catalyst

The electrical properties of bisphenol A type epoxy resin (1) cured with tris(salicylaldehydato) aluminum/diphenylsilanediol [(1)-Al(SA)₃/DP] were compared with that cured with BF_3 monoethylamine complex catalyst [(1)- BF_3 -MEA]. Figure 2 shows the relation between dissipation factor ($\tan \delta$) and temperature measured. The dissipation factor of (1)- BF_3 -MEA increased remarkably at the temperature above 130°C. However, in the case of (1)-Al(SA)₃/DP, the value had a maximum at about 150°C and increased again gradually at temperature above 200°C. The maximum point shifted to higher temperature and the height of peak diminished when (1)-Al(SA)₃/DP was after-cured at 180°C for 15 h. Figure 2 also shows the modulus of elasticity. T_g of (1)-Al(SA)₃/DP coincided with the maximum temperature for $\tan \delta$ -temp-



Scheme 1. Electrode structure.

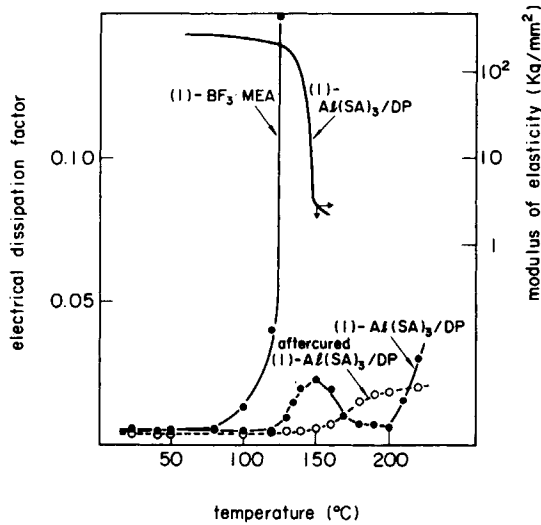


Fig. 2. Relation between electrical dissipation factor and temperature, and relation between modulus of elasticity and temperature. Sample, thickness 1 mm, (1)-Al(SA)₃/DP, Al(SA)₃, 2 phr, DP, 2 phr, (1)-BF₃·MEA, BF₃·MEA, 3 phr, 150°C, 15 h, aftercure, 180°C for 15 h; the frequency for tan δ measurement is 50 Hz.

erature curve. Therefore, the peak is considered to be due to the mobility of main chain of epoxy resin cured. The dissipation factor for (1)-BF₃·MEA did not have such a maximum. This could be explained as follows: The conductance loss became a dominant factor at temperatures above 130°C; therefore, the original peak of tan δ due to the main chain mobility was considered to be buried by the increase in the conductance loss.⁴

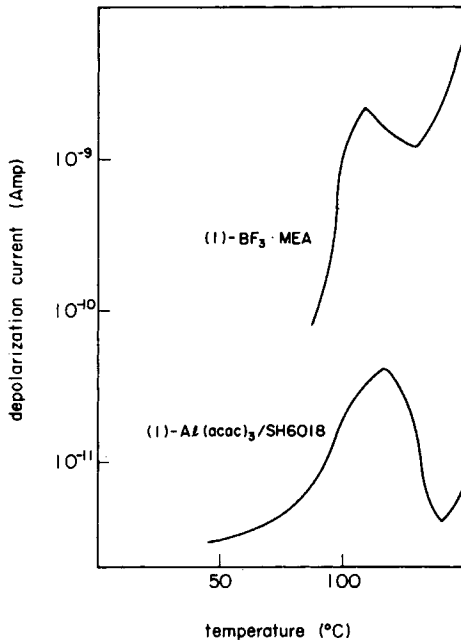


Fig. 3. Depolarization current curve. Experimental conditions, see Figure 4.

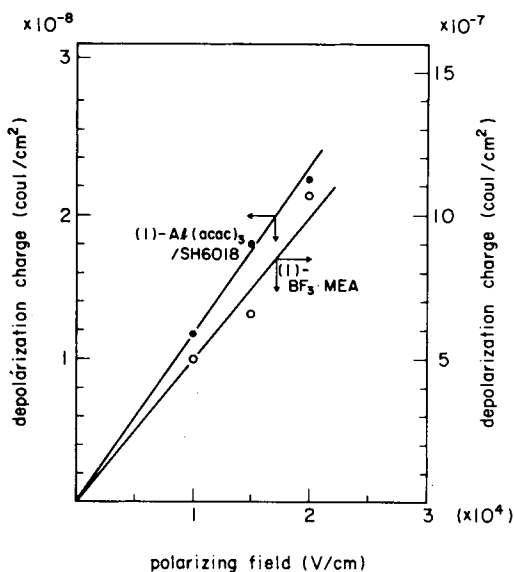


Fig. 4. Relation between depolarization charge and polarizing field. Thickness 1 mm; (1)-Al(acac)₃/SH6018, Al(acac)₃, 2 phr, SH6018, 3 phr, 150°C, 15 h, electrode, 10 mm- ϕ , 2×10^4 V/cm at 150°C.

The difference in the electrical properties between (1)-Al(acac)₃/SH6018 and (1)-BF₃-MEA was investigated by means of thermal depolarization current method.⁵ Figure 3 shows the depolarization current-temperature curve. The curves had a maximum at about 120°C. Figure 4 shows the relation between the depolarization charge (Q) and the polarizing field (E_p). The depolarization charge for (1)-Al(acac)₃/SH6018 was about 10^{-8} C/cm² and that for (1)-BF₃-MEA was about 10^{-7} C/cm². Generally speaking, polarization of dielectric was divided into heterogeneous polarization and homogeneous polarization.⁶ In the former, there are heterocharge, which is caused by the macroscopic shift of ionic impurity in dielectric, and homocharge, which is caused by the injection of charge from electrode to dielectric. In the latter, there are orientational polarization charge and heterocharge, which is caused by the microscopic displacement of ionic impurity. In the present experiment, the charge was hetero. The depolarization charge was directly proportional to the polarizing field. Therefore, the charge was considered to be due to homogeneous polarization.⁷ If the polarization is attributed to the thermal disorder for orientational dipole only, maximum value for orientational polarization charge would be obtained from the following equation by use of Debye's polarization orientation theory⁸:

$$P = N\mu_{eff}^2 E_p / 3kT_p,$$

where N = the number of dipoles in 1 cm³, μ_{eff} = effective dipole moment, E_p = polarizing field, k = Boltzmann's constant, T_p = depolarization temperature. Hydroxide and ether linkage are present as the dipole in the cured epoxy resins. The effective dipole moment for alcohol and ether is about 1.6-1.7 Debye. The calculated orientational polarization charge was about 10^{-10} C/cm². The measured depolarization charge was more than the calculated depolarization charge by a factor of about 10^2 in case of (1)-Al(acac)₃/SH6018 and by a factor

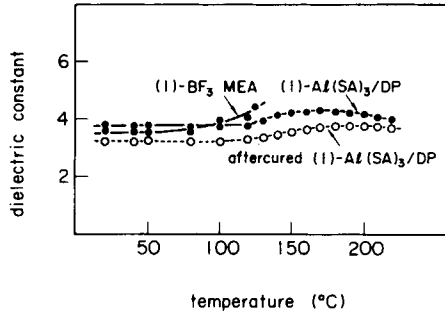


Fig. 5. Relation between dielectric constant and temperature. Aftercure, 180°C for 15 h, dielectric constant of (1)-BF₃-MEA above 130°C could not be measured.

of about 10^3 in case of (1)-BF₃-MEA. Therefore, the depolarization charge could not be explained in terms of thermal disorder for orientational dipole only. However, when microscopic displacement and trap for ionic impurity were considered, the experimental results could be explained. Both of (1)-Al(acac)₃/SH6018 and (1)-BF₃-MEA had ionic impurity; however, it was found that the amount of ionic impurity in (1)-Al(acac)₃/SH6018 was smaller than that in (1)-BF₃-MEA. The dielectric constant for (1)-Al(SA)₃/DP relatively remained constant throughout the temperature from 25°C to 220°C.

Figure 6 shows the relation between volume resistivity and temperature. The volume resistivity of (1)-Al(SA)₃/DP was higher than that of (1)-BF₃-MEA by a factor of about 10^4 times at 150°C. The volume resistivity for (1)-Al(SA)₃/DP hold the value of 10^{12} Ω·cm at even 200°C.

Breakdown voltage for (1)-Al(SA)₃/DP was compared with that for (1)-BF₃-MEA. Figure 7 shows the results. The breakdown voltage for (1)-Al(SA)₃/DP increased gradually with temperature; however, that for (1)-BF₃-MEA decreased considerably at 120°C. These results show that Al(SA)₃/DP

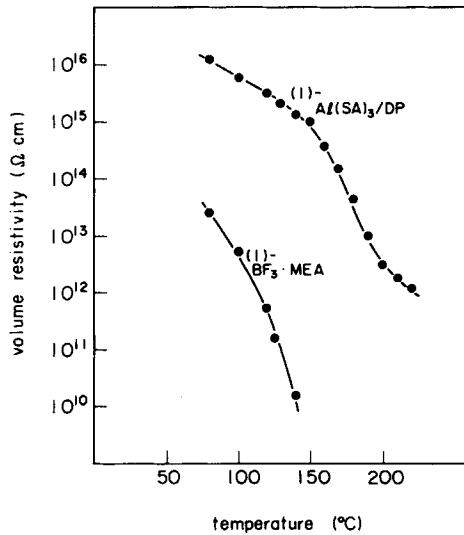


Fig. 6. Relation between volume resistivity and temperature.

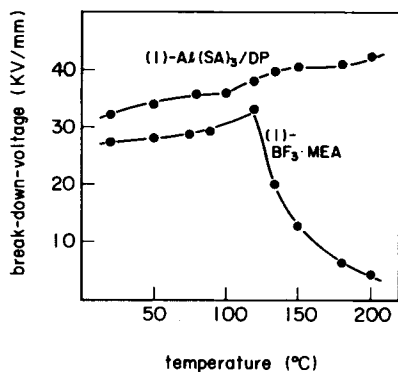


Fig. 7. Relation between breakdown voltage and temperature.

catalyst system is "clean" electrically, compared with BF_3 -complex catalyst. The difference of electrical properties between $\text{Al}(\text{SA})_3/\text{DP}$ and BF_3 -complex can be explained as follows.

The polymerization by use of $\text{Al}(\text{SA})_3/\text{DP}$ catalyst was considered to be caused cationically by the proton formed by the interaction between aluminum complex and silanol as follows.⁹ Diphenylsilanediol was consumed by self-condensation reaction, condensation with secondary alcohol in epoxy resin, and addition to the epoxide during polymerization, as shown in Figure 9.^{3,8} The cationic site is made by the interaction between aluminum complex and silanol. If the silanol is consumed during the polymerization reaction, no cationic site will exist in the polymerization system. Therefore, excellent electrical properties of (I)- $\text{Al}(\text{SA})_3/\text{DP}$ catalyst are due to the absence of ionic species in the cured resin matrix.

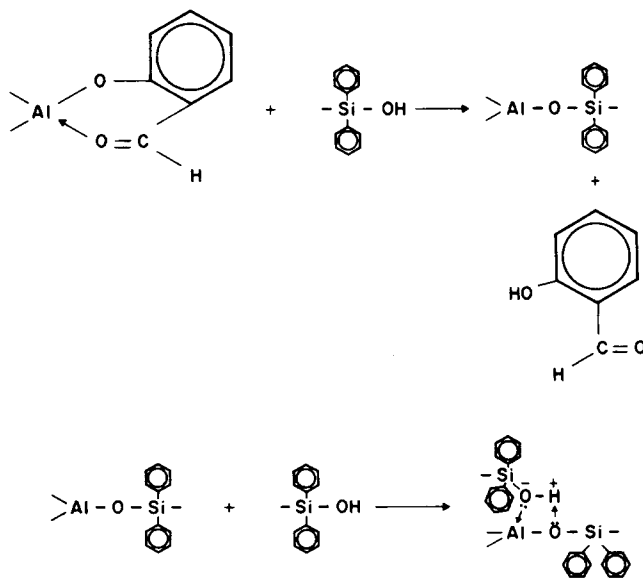


Fig. 8. Active site of $\text{Al}(\text{SA})_3/\text{DP}$ catalyst.

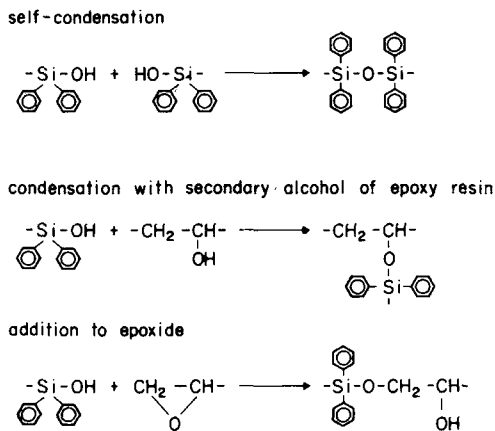


Fig 9. Consumption of silanols.

On the other hand, when epoxy resin is cured by BF_3 -complex, BF_3 is varied in the cured resin matrix and becomes the ionic impurity which damages the insulation properties. The absence of any appreciable ionic species after polymerization will be important for the excellent electrical properties.

The presence of the cationic site in the cured resin matrix was considered to affect the thermal stability. The relation between weight loss of the cured resin plate and the aging time at 225°C is shown in Figure 10. The ratio of weight loss for (1)- BF_3 -MEA was larger than that for (1)- $\text{Al}(\text{SA})_3/\text{SH6018}$ (Toray silicone, silicone resin containing SiOH , OH equivalent 400). Ionic species in (1)- BF_3 -MEA would accelerate the decomposition of the polymer chain.

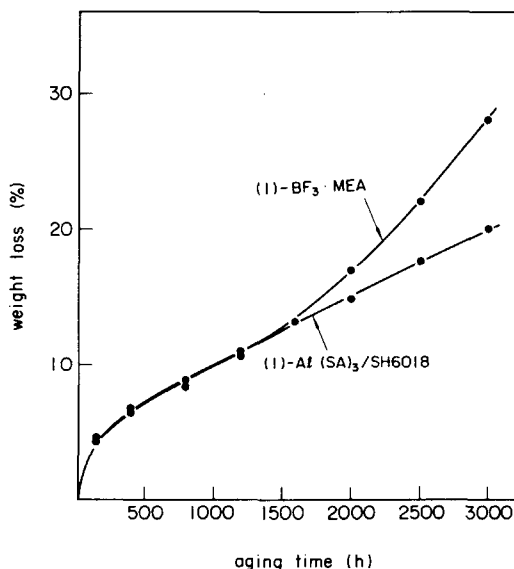


Fig. 10. Relation between weight loss and aging time at 225°C . Sample, (1)- $\text{Al}(\text{SA})_3/\text{SH6018}$, $\text{Al}(\text{SA})_3$, 2 phr, SH6018, 2 phr, 150°C , 15 h, $1 \times 10 \times 10$ mm.

TABLE I
Electrical Properties for Epoxy Resin Cured with Aluminum Complex/Silanol Catalysts^a

Al complex	(phr)	Silanol	phr	Dissipation factor (%)		Dielectric constant		Volume resistivity ($\Omega\cdot\text{cm}$) at 220°C
				25°C	220°C	25°C	220°C	
Al(SA) ₃	2.4	Ph ₃ SiOH	3.8	0.5	1.2	3.7	3.8	7.2 × 10 ¹²
Al(Etaa) ₃	2.6	Ph ₃ SiOH	3.8	0.4	2.9	3.9	4.1	3.0 × 10 ¹²
Al(acac) ₃	2.0	Ph ₃ SiOH	3.8	0.5	6.0	3.7	4.4	9.5 × 10 ¹¹
Al(SA) ₃	2.4	Sh6018	5.6	0.5	2.5	3.8	3.9	5.0 × 10 ¹²
Al(SA) ₃	2.4	Ph ₂ Si(OH) ₂	3.0	0.5	3.0	3.8	4.0	1.1 × 10 ¹²
			1.5	0.8	12.4	3.9	6.1	—
			3.0	0.6	8.0	3.7	4.9	—
			4.5	0.7	6.2	3.7	4.5	—
Al(acac) ₃	2.0	Ph ₂ Si(OH) ₂	6.0	0.7	4.9	3.7	4.0	—
			7.5	0.5	5.7	3.9	4.7	—
			9.0	0.9	10.0	4.1	5.7	—

^a 150°C for 15 h cure; Epikote 828.

Dependence of the Electrical Properties on Structure of Catalyst

The electrical properties depend on the structure of catalyst, as shown in Table I. When triphenylsilanol was used as the silanol component, the electrical properties at 220°C deteriorated, depending on the structure of catalyst, as follows: $\text{Al}(\text{SA})_3 > \text{Si}(\text{Etaa})_3 > \text{Al}(\text{acac})_3$. Gellation of the epoxide grew late, depending on the catalyst, in the following order: $\text{Al}(\text{SA})_3/\text{Ph}_3\text{SiOH} > \text{Al}(\text{Etaa})_3\text{SiOH} > \text{Al}(\text{acac})_3/\text{Ph}_3\text{SiOH}$. The electrical properties improved when curing proceeded.

When $\text{Al}(\text{SA})_3$ was used as the aluminum component, the dependence of electrical properties on the silanol structure was examined. The electrical properties at 220°C lowered as follows: $\text{Ph}_3\text{SiOH} > \text{SH6018} > \text{Ph}_2\text{Si}(\text{OH})_2$. The order could be explained as the same way.

Dependence of the electrical properties on the amount of the catalyst was examined. When the amount of the silanol increased, the gellation time of the epoxy resin grew fast. However, most excellent electrical properties were obtained in case of aluminum complex/silanol (1/3) (mol/mol). When the ratio of the silanol was much too large, silanol would remain in the matrix of the cured epoxy resin; therefore, the electrical properties would deteriorate.

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