

Development of Epoxy Resin with Low Dielectric Property

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Abstract

The significant progress in recent communications network technology has enabled the development of epoxy resins with low dielectric properties to utilize high frequency bands for application to electrical/electronic devices. By exploiting the molecular design technology of Nippon Steel Chemical & Material Co., Ltd., a novel epoxy resin has been developed whose component is based on a naphthalene backbone. Using a cured product with phenol novolac as a hardener, the properties required for electronic materials and low dielectrics have been achieved by introducing the naphthalene backbone and decreasing the concentration of epoxy units as the polar group. The application of this matrix resin to a corresponding high frequency multi-layer print circuit board and the substrates for semiconductor mounting is promising.

1. Introduction

Epoxy resin is a common term for resins with a molecular weight distribution having multiple three-membered cyclic ethers, generally called oxirane rings, in the molecules and has been widely used in paints, adhesives, and composite materials. Particularly in the electronic material field, the use of epoxy resins in electronics board laminates and IC encapsulants has expanded rapidly since the 1980s. In circuit board applications and semiconductor packaging materials, which continue to evolve, there have been advances in the use of low-modulus resins and compound technology for using high thermal conductivity epoxy resins and fillers to meet the demands of dimensional stability, such as low warpage and heat dissipation due to the increase in the power module application, contributing to the advancement of electronic devices.

Similarly, in the information and communication fields, AI technology is evolving at a rapid pace, and the processing speed of computing devices such as CPUs and GPUs, as well as the amount of signal transmission, are increasing dramatically. This situation means that the epoxy resins that have been commonly used up until now have reached their limits and that new epoxy resins are desired in their place.

In this report, we introduce the development of epoxy resins designed with a focus on dielectric properties, which are important physical properties in the electronics for information and communications field.

2. Development of Low Dielectric Epoxy Resin

2.1 Design policy

The calculation speed depends on the clock speed (f : frequency) of the mounted semiconductor device. The output speed between packages through the printed wiring board depends on the signal transmission speed on the printed wiring board. Both of these speeds depend on the dielectric constant ε and the dielectric loss tangent δ and are expressed by the following two equations.

$$T_d = l \cdot \sqrt{\varepsilon/c} \quad (1)$$

where T_d is the delay time, l is the transmission distance, and c is the speed of light.

$$\text{Dielectric loss} \propto \sqrt{\varepsilon \cdot f \cdot \tan \delta} \quad (2)$$

where f is the frequency and $\tan \delta$ is the dielectric loss tangent, which represents the loss from electrical energy to thermal energy when an AC electric field is applied to the material. As expressed by the Clausius-Mossotti equation,¹⁾ ε is proportional to the value of (molar polarizability)/(molar volume) and depends on the amount of polarization due to polar groups in the resin and the number of molecules per unit volume. On the other hand, the loss of thermal energy for the dielectric loss tangent is determined by the magnitude and mobility of the dipole moment in the molecule. Different to low-molecular weight materials, when interactions such as intermolecular stacking and orientation exist in polymer materials, the dielectric loss tangent tends to decrease due to the cancellation of dipole moments in the mesoscopic region and the decrease in the mobility of the polymer chain.²⁾

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Considering this phenomenon, we aimed to reduce the polarity of epoxy resins and the mobility of polymer chains. We came up with the idea and design of a naphthol aralkyl epoxy resin, as shown in Fig. 1. The structural formula of the naphthol aralkyl resin designed this time is shown in Table 1. The concept is to reduce the concentration of polar groups in the network polymer by introducing a naphthalene ring, which is a condensed ring structure, into the resin and to reduce molecular mobility by improving the rigidity of the condensed ring structure. Using the Entry No. 1 sample as the basis, we designed a resin in which the substituents were changed from epoxy groups to others in order to reduce the secondary alcoholic hydroxyl groups generated after the crosslinking reaction. The resin obtained was named the Entry No. 2 sample. The reference materials used to verify the effect of the naphthalene structure were a phenol aralkyl resin that does not contain naphthalene and a cresol novolac resin that is commonly used in electronic materials. The curing agent was a phenol novolac resin with a softening point of 89°C. The epoxy equivalent and the phenolic hydroxyl group equivalent were adjusted to 1:1. As a curing accelerator, 2-ethyl-4-methyl-

imidazole was used. After kneading the various raw materials with a heated roll, they were molded by a transfer mold process at 175°C for 5 min, demolded, and heat treated at 200°C for 5 h as a post-cure to produce a cured product. These cured products were subjected to various thermal analyses and dielectric measurements using a capacitance method (1 GHz).

2.2 Synthesis of epoxy resins containing naphthol aralkyl skeleton

Naphthol aralkyl epoxy resin (4) can be obtained by dehydrating the epoxy resin precursor (3) with epichlorohydrin under an alkaline condition, whereas (3) is obtained by reacting the raw material 1-naphthol (1) with a xylylene compound (2) capable of promoting electrophilic reactions. The resin used in the Entry No. 2 sample was synthesized by partially capping the hydroxyl groups of the precursor (3) and then epoxidizing the precursor. This method allows the molecular weight of (4) to be adjusted arbitrarily by changing the molar ratio of (1) and (2). In this report, epoxy resins were synthesized to adjust the molecular weight with a softening point (ring and ball method) of 75°C based on JIS K 7234 and evaluated as the Entry No. 1 and No. 2 samples.

2.3 Properties of cured epoxy resins with naphthol aralkyl skeleton

Table 2 shows the properties of the cured products of the two naphthol aralkyl type epoxy resins used in this evaluation, as well as the phenol aralkyl type epoxy resin and the cresol novolac type epoxy resin used as comparative materials. The glass transition temperature Tg value was almost dependent on the epoxy equivalent (WPE = weight per epoxy equivalent) of the phenolic hydroxyl group of the phenolic novolac resin and the epoxy group of the epoxy resin. The more crosslinking points there were per unit weight (= unit volume) in the cured product, the higher the Tg value was. It is interesting to note that in the phenol aralkyl type resin shown in the ref. No. 1 sample in Table 1, the epoxy equivalent was slightly lower (= more crosslinking points), but the Tg value tended to be slightly lower than that. This phenomenon indicates that the struc-

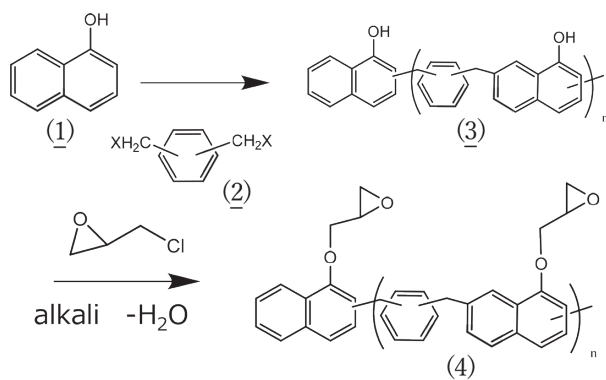


Fig. 1 Synthesis scheme of naphthol aralkyl epoxy resin

Table 1 Molecular structure of epoxy resin and hardener in this investigation

	No.	Structure		
		Epoxy resin		Hardener
Entry	1		R:	
	2		R: or substituted	
Ref.	1			
	2			

ture in which the benzene rings are crosslinked with the xylene structure in the main skeleton makes it easier to disentangle the molecular chains in the cured product in the same temperature range than the structure using the naphthalene ring, which is a condensed ring structure.

A similar consideration can be confirmed for the linear expansion coefficient α_1 in the glass region. That is, the linear expansion coefficient α_2 in the rubber region where the molecular chains are untangled shows similar values for all resins. In the situation where the molecular motion is confined in the glass region, the molecular motion is restricted. Therefore, the resin into which the naphthalene ring with a rigid structure is introduced has a lower α_1 value.

Regarding the moisture absorption rate, the Entry No. 1 and No. 2 sample resins with the naphthalene ring introduced exhibited a lower moisture absorption rate than the comparative materials, even taking into account their high epoxy equivalent.

The moisture absorption rate of a general polymer depends greatly on the structure and concentration of polar groups contained in the polymer. Particularly, the presence of hydroxyl groups, which have a high affinity for water molecules, greatly affects the moisture absorption rate of the polymer.

It can be assumed that the reaction between epoxy groups and phenolic hydroxyl groups generates secondary alcoholic hydroxyl groups, affecting the moisture absorption rate. By reducing the number of epoxy groups in the resin, decreasing the concentration of secondary alcoholic hydroxyl groups in the cured material, and introducing rigid and highly hydrophobic naphthalene rings into the molecular chains in the cured material, it was possible to achieve a significantly lower moisture absorption rate than that of commonly used cresol novolac epoxy resins.

Low moisture absorption is very important for electronic materials. For example, in circuit board applications and semiconductor encapsulation materials, electronic components are mounted using solder. In surface mounting applications, the mainstream method is to print solder on the circuit beforehand, then mount electronic components on the circuit board, and then place the board into an infrared oven using a belt conveyor, etc., and solder the components by radiative heat transfer. In lead-free soldering, the temperature during mounting rises to about 260°C. If the material absorbs moisture, the moisture contained in the material will vaporize and expand all at

once, destroying the material itself and delaminating the metal contact part, which is the conductor, and greatly affecting the yield of electronic components. In addition, moisture also affects the migration of ion components in the material under high temperature and high humidity conditions and also influences component reliability, such as insulation failure. This resin, which has a naphthalene skeleton, is an epoxy resin but has low moisture absorption, so it is expected to be suitable for use in the circuit board application and semiconductor encapsulation application.

Finally, regarding the dielectric properties, the dielectric constant (D_k) depends on the molar polarizability and molar volume, as mentioned above. The dielectric loss (D_f) depends on the magnitude of the dipole moment in the molecule. In both cases, the lower the concentration of polar groups in the cured product, the lower the dielectric constant and dielectric loss tend to be. When the epoxy resin is cured with the phenol novolac resin, the secondary alcoholic hydroxyl groups that are generated become polar groups and affect the dielectric properties. **Figure 2** shows the measurement results of D_k , D_f , and T_g . Regarding D_k , all resins showed almost the same dielectric constant. This finding suggests that the contribution of molar polarizability/molar volume is hardly affected even if the naphthalene skeleton is introduced. On the other hand, a clear decrease was observed in the dielectric loss when the naphthalene ring was intro-

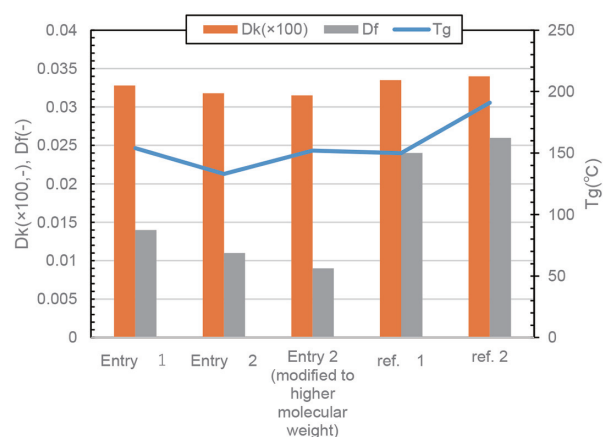


Fig. 2 Comparison with T_g and dielectric properties of each epoxy resin

Table 2 Weight per epoxy equivalent of raw epoxy resins and the properties of cured products

Epoxy resin	Entry		Ref.	
	No. 1	No. 2	No. 1	No. 2
Feature in structure	α -naphthol aralkyl type	α -naphthol aralkyl type (low concentration of epoxy moiety)	Phenol aralkyl type	o-cresol novolac type
Weight per epoxy equivalent (g/eq.)	275	325	250	202
T_g ($^\circ\text{C}/\text{TMA}$)	154	136	150	191
α_1 (ppm/ $^\circ\text{C}$)	45	45	54	56
α_2 (ppm/ $^\circ\text{C}$)	168	170	168	171
Moisture absorption* (wt.%)	0.70	0.64	1.07	1.69
D_k (-, 1 GHz)	3.28	3.18	3.35	3.40
D_f (-, 1 GHz)	0.014	0.011	0.024	0.026

* treated under the conditions of 85°C, 85%, 100 hrs

duced. A possible reason is that the introduction of the naphthalene ring restricts the mobility of the polymer chain, resulting in less loss toward thermal energy. Also, in the Entry No. 2 sample, a decrease in the dielectric loss tangent was observed. This decrease indicates that the dielectric loss tangent can also be reduced by reducing the polar groups.

Here, the T_g decreases as the number of epoxy functional groups decreases. In order to overcome this disadvantage of the Entry No. 2 sample, the molar ratio of the precursor in the Entry No. 2 sample was changed. A resin with a higher molecular weight and lower mobility of the molecular chain was designed. When we similarly cured the designed resin with phenol novolac, we succeeded in creating a resin that simultaneously improved the T_g and reduced the dielectric loss tangent. In this study, we used the phenol novolac resin as the curing agent. By using a curing agent called an active ester type³⁾ that does not generate secondary alcoholic hydroxyl groups, which become polar groups in the cured material, we can expect to reduce the dielectric properties further and apply the obtained epoxy resin to high-frequency compatible substrates.

3. Conclusions

To keep pace with the rapid progress in electronics for the information and communications field, we focused on a naphthol aralkyl resin as a molecular design aimed at low dielectric properties. We designed a resin in which the number of epoxy groups was controlled by partially capping the hydroxyl groups of the precursor. When cured with a phenol novolac resin, the epoxy resin exhibited a low linear expansion coefficient, low moisture absorption, and low dielectric properties compared to the cresol novolac resin and phenol aralkyl resin, which do not have naphthalene rings. In addition, although there was no clear difference in the dielectric constant, a significant decrease in the dielectric loss tangent was observed with the introduction of naphthalene rings. These unique characteristics can contribute to the future progress of electronic materials. We will continue to work on new molecular designs to meet the demands of further evolution.

References

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