

Development and Applications of Functional Phenolic Resins

TAKEMURA Kazuya*¹ NAKAO Hiroaki*²

Abstract:

Regarding three types of functional phenolic resins (Trisphenolmethane resin, Dicyclopentadiene type phenolic resin, Benzoxazine) commercialized by JFE Chemical and two types of developed products, heat resistance, dielectric properties, transparency, and the compatibility of rubber for tires were compared with the conventional phenol resin. The glass transition temperature of Trisphenolmethane resin is 35°C higher than that of conventional resin, the dielectric constant and dielectric loss tangent of dicyclopentadiene type phenol resin are 20% lower than that of conventional resin, and thermal decomposition temperature of Benzoxazine is 54°C higher than that of conventional resin and the dielectric loss tangent of Benzoxazine is 1/5 of that of conventional resin. In addition, the developed products have excellent transparency and compatibility with rubber, which is a material for tires. These functional phenolic resins are useful for a sealing material for power device of EVs and hybrid vehicles that require high heat resistance, a circuit board material for engine control units, an additive for reinforcing automobile tires, and a material for circuit boards of 5G smartphones and communication devices of mobile phone base stations that requires low dielectric properties.

1. Introduction

Phenolic resins were the world's first artificial synthetic resins, and are generally manufactured by condensation polymerization of phenol and formaldehyde. Phenolic resins are broadly classified as novolacs, which are synthesized using an acid catalyst, and resols, which are synthesized with an alkali catalyst. The cured products produced by reacting a phenolic resin with an epoxy resin or an amine hardener possess excellent

electrical properties and high heat resistance, and are currently used in a wide range of applications, including housings for electrical equipment, machine parts, resins for circuit boards, semiconductor sealing materials, binders for foundry sand, tire reinforcing resins, adhesives and feedstocks for epoxy resins, among others.

On the other hand, various properties which cannot be satisfied with conventional phenolic resins have been required in the automotive and electronic equipment fields in recent years. For example, in sealing resins for power devices (power semiconductors) used in electric vehicles (EVs) and hybrid vehicles, high heat resistance capable of withstanding the high operating temperatures of 200 °C or more of next-generation devices is required, while long-term heat deterioration resistance under high temperature environments is necessary in the circuit board resin of automotive engine control units, and the phenolic resins used to reinforce automobile tires must provide improved compatibility with rubber and fuel economy. In non-automotive fields, in the field of electronic equipment, low dielectric properties are necessary in resins for circuit boards and semiconductor sealing resins in order to reduce transmission loss and signal delay in high speed, large capacity telecommunications equipment such as 5G smartphones and servers for mobile phone base stations.

In order to effectively utilize the phenols contained in coal tar and achieve the advanced property requirements demanded in recent years, JFE Chemical is promoting commercialization of functional phenolic resins with different molecular structures from those of the conventional phenolic resins. To date, we have commercialized three types of functional phenolic resins, that is, trisphenol methane resin, dicyclopentadiene type phenolic resin and benzoxazine resin, and have

† Originally published in *JFE GIHO* No. 47 (Aug. 2021), p. 31–36



*¹ Fine Chemicals R&D Center,
Chemical Research Laboratory,
JFE Chemical



*² Manager,
Commercialization Promotion Sec.,
Fine Chemicals Dept.,
JFE Chemical

also developed two types of special phenolic resins as dicyclopentadiene type derivative products. These materials have the potential to satisfy the advanced property requirements of recent years.

This report compares the physical properties of cured products of the above-mentioned three types of functional phenolic resins and two developed products, and introduces promising applications for these functional phenolic resins in the fields of EVs and hybrid vehicles and electronic equipment.

2. Properties and Applications of JFE Chemical's Functional Phenolic Resins

2.1 Trisphenol Methane Resin

Trisphenol methane resin is a functional phenolic resin which is obtained by condensing phenol and a hydroxybenzaldehyde in the presence of an acid catalyst¹⁾. In the molecular structure, one of the methylene hydrogen groups of the conventional novolac type phenolic resin (**Fig. 1**) is substituted with a hydroxyphenyl group (**Fig. 2**). Although the hydroxyl group concentration does not differ greatly from that of conventional phenolic resin, thermal motion of the molecules is more difficult to occur than in the novolac type phenolic resin due to the increase in the bulky hydroxyphenyl group, resulting in improved heat resistance.

Table 1 shows a comparison of the glass transition temperatures of products obtained by thermal curing using the developed trisphenol methane resin and a novolac type phenolic resin as the hardener of a general purpose epoxy resin (ortho-cresol novolac type). When the trisphenol methane resin was used, the glass transition temperature of the cured product was 195 °C, which is 35 °C higher than the 160 °C of the cured product obtained with the conventional novolac type

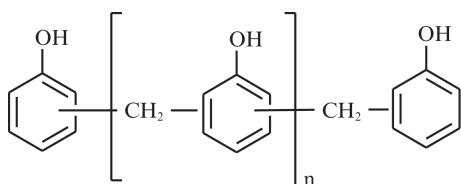


Fig. 1 Novolac type phenolic resin

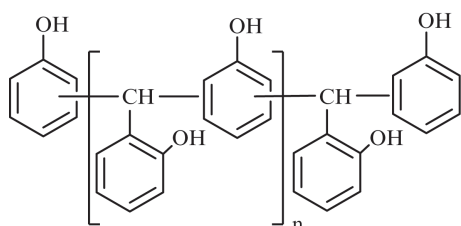


Fig. 2 Trisphenol methane resin

phenolic resin. Increasing the glass transition temperature suppresses deformation, swelling and deterioration of members at high temperatures, and thus improves durability and reliability when members are used in high temperature environments.

As one application of trisphenol methane resin in EVs and hybrid vehicles, sealing materials for power devices may be mentioned. Power devices are used to perform frequency conversion, direct/alternating current conversion and voltage conversion of electric power in EVs and hybrid vehicles, and improvement of their conversion efficiency is important for energy saving in the vehicles. Silicon devices are widely used in the present generation of power devices, but because their conversion efficiency is approaching its upper limit due to the use of increasingly large currents, a changeover to SiC (silicon carbide) devices, which are next-generation high efficiency power conversion devices, is foreseen in the future²⁾. Since SiC devices operate efficiently at operating temperatures of 200 °C and higher, high heat resistance is required in the sealing resin of these devices³⁾.

Trisphenol methane resin is considered to be one material that can achieve the glass transition temperatures of 200 °C and higher demanded in sealing materials for SiC power devices when used as the hardener for high heat resistance epoxy resins. It is also useful in materials for the circuit boards of engine control units, which are installed in the high temperature environment of the engine compartment. In comparison with the conventional resin, the higher glass transition temperature of the developed resin is expected to improve the stability of strength and durability in long-term use in high temperature environments.

JFE Chemical has commercialized trisphenol methane resin (S-TPM Series) in which salicylaldehyde and phenol are used as the feedstocks, and can supply products in three grades with different softening points (103 °C, 113 °C, 130 °C).

2.2 Dicyclopentadiene Type Phenolic Resin

Because high speed, large volume data processing is necessary in the circuits of telecommunications equip-

Table 1 Glass transition temperature of cured product of ortho-cresol novolac epoxy resin and phenolic

Epoxy resin	Ortho-cresol novolac epoxy resin	
	Epoxy equivalent (g/eq)	223
Phenolic resin (hardener)	Novolac epoxy resin	Trisphenol methane
	Hydroxy group equivalent (g/eq)	101
Glass transition temp. of cured product (°C)	160	195

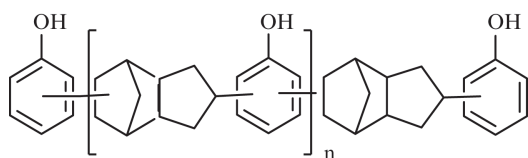


Fig. 3 Dicyclopentadiene type phenolic resin

ment such as 5G smartphones and mobile phone base stations, a high frequency current circuit signals are used. Although use of a high frequency current is effective for large volume information processing, transmission loss and signal delay occur easily. To prevent these problems, it is necessary to use materials with a low dielectric constant and low dielectric tangent in peripheral resin parts such as circuit boards⁴⁾. In response to this need, JFE Chemical commercialized a dicyclopentadiene type phenolic resin with a low dielectric constant and low dielectric tangent in comparison with conventional phenolic resins.

The chemical structure of the dicyclopentadiene type phenolic resin consists of alternating copolymers of phenol and dicyclopentadiene, as shown in Fig. 3⁵⁾, and its degree of polymerization is approximately 7 or less.

The conventional novolac type phenolic resin (Fig. 1) synthesized from phenol and formaldehyde consists of two phenol groups bonded by a methylene group having a carbon number of 1, and has a high concentration of phenolic hydroxyl groups, which have large electrical bias. Therefore, its dielectric constant and dielectric tangent are high owing to its high resin polarity, and application to circuit board materials for high frequency current is limited.

In contrast, in the developed dicyclopentadiene type phenolic resin (Fig. 3), two phenol groups are bonded by a dicyclopentadiene group, which has a carbon number of 10, and the concentration of hydroxyl groups is low, at about 45 %, in comparison with the conventional phenolic resin, and the polarity of the resin is also low. As a result, cured products display the distinctive features of a low dielectric constant and low dielectric tangent. In comparison with the general novolac type phenolic resins, the dielectric constant and dielectric tangent of products produced by thermal curing using the dicyclopentadiene type phenolic resin are reduced by approximately 20 % (Table 2). Moreover, it is known that epoxy resins in which the dicyclopentadiene type phenolic resin is used as a feedstock also show low dielectric properties and excellent heat resistance⁶⁾.

When the dicyclopentadiene type phenolic resin is used, the dielectric properties of the cured product decrease as the molecular weight increases. This is con-

Table 2 Properties of cured products of epoxy resin and hardeners

Epoxy resin	Ortho-cresol novolac	
Epoxy equivalent (g/eq)	223	
Hardeners (phenolic resin)	Novolac	Dicyclopentadiene type
Hydroxy group equivalent (% mol/g)	0.99	0.55
Hydroxy group equivalent (g/eq)	101	181
Relative permittivity (1 GHz)	3.43	2.80
Loss tangent (1 GHz)	0.034	0.026

sidered to be the result of a decrease in the terminal phenolic hydroxy groups at higher molecular weights. Furthermore, since the dicyclopentadiene group is a rigid cyclic molecule, thermal movement of the molecules is difficult and the heat resistance of the cured products is also high, and as one of advantages, water absorption is low due to the low polarity of the resin.

The dicyclopentadiene type phenolic resin is produced by condensation of dicyclopentadiene and an equimolar or higher phenol in the presence of an acid catalyst. As production processes, a method using a boron trifluoride phenol complex or other homogeneous acid catalyst⁷⁾ and a method using a heterogeneous catalyst such as a film-type or bead-type cation exchange resin⁸⁾ are known. In the homogeneous acid catalyst method, the catalyst which has dissolved in the reaction liquid is removed after completion of the reaction, but it is necessary to adsorb the catalyst on an inorganic adsorbent and then remove the catalyst by filtering the adsorbent in a time-consuming filtration process. The heterogeneous catalyst method eliminates the need for filtration of the catalyst adsorbent, as the cation exchange resin in film or bead form is simply filled in a circulating type catalyst tank and the reaction liquid is then circulated.

2.3 Dicyclopentadiene *p*-Cresol Condensation polymer (Developed Product)

The dicyclopentadiene type phenolic resin has a reddish-brown color and also causes remarkable coloration of cured products (Fig. 4 (a)), making it difficult to use in applications in which transparency is required. However, in the developed product, dicyclopentadiene *para*-cresol (*p*-cresol) condensation polymer (Fig. 5), *p*-cresol is used in place of phenol and is alternately polymerized with the dicyclopentadiene, resulting in a light color and excellent transparency⁹⁾. *p*-cresol has a methyl group at the *para* position of a phenolic hydroxy group, and it is thought that transparency is improved because direct oxidation of the *para* position of the aromatic ring is difficult and formation of col-



(a) Cured product of alicyclic epoxy resin and dicyclopentadiene type phenolic resin (Light transmittance = 34%) (3.5 mm thickness)
 (b) Cured product of alicyclic epoxy resin and dicyclopentadiene *p*-cresol resin (Light transmittance = 76%) (3.5 mm thickness)

Fig. 4 Light transmittance of cured products

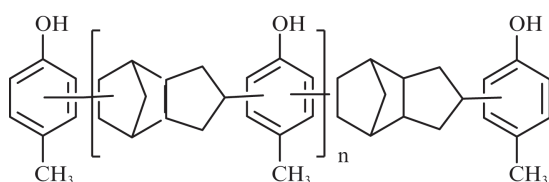


Fig. 5 Dicyclopentadiene *p*-cresol resin

ored oxides such as benzoquinones, etc. is suppressed. Cured products with high transparency, low dielectric properties and excellent heat resistance were obtained when this resin was used as a hardener for alicyclic epoxy resin (Fig. 4 (b)).

Because the developed dicyclopentadiene *p*-cresol condensation polymer can improve transparency while maintaining the low dielectric properties and low moisture absorption of the dicyclopentadiene type phenolic resin, this resin can be used in applications such as transparent sealing materials for light emitting diodes (LEDs), etc. and materials for photocuring resins and photosensitive resins, etc.

2.4 Cashew Oil Modified Dicyclopentadiene Type Phenolic Resin (Developed Product)

Phenolic resins are added to some parts of automotive tires to reinforce stiffness and strength¹⁰⁾. However, the natural rubber and synthetic rubber used as the material for tires are aliphatic molecules, and in some cases it is difficult to obtain an adequate effect of phenolic resin addition due to poor compatibility between the rubber and the phenolic resin, which is an aromatic.

JFE Chemical developed cashew oil modified dicyclopentadiene type phenolic resin as a phenolic resin for reinforcement of automobile tires. This resin has excellent compatibility with rubber and also contributes to improved fuel economy.

The developed cashew oil modified dicyclopentadiene type phenolic resin was synthesized by chemically bonding the aromatic rings of dicyclopentadiene type phenolic resin with the intramolecular double bonds of cashew oil by an electrophilic substitution reaction in

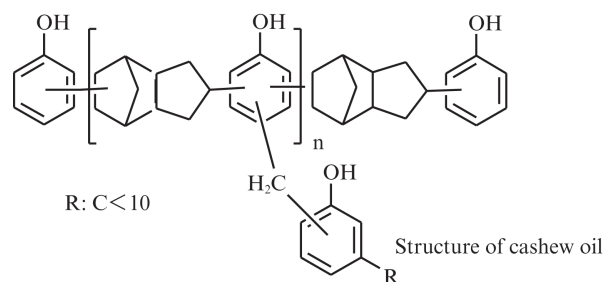


Fig. 6 Chemical structure of cashew oil modified dicyclopentadiene type phenolic resin (1)

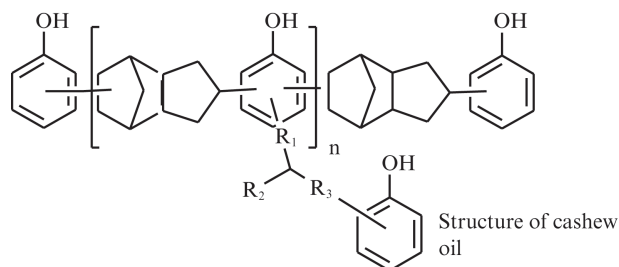


Fig. 7 Chemical structure of cashew oil modified dicyclopentadiene type phenolic resin (2)

the presence of an acid catalyst¹¹⁾. **Figures 6 and 7** show the chemical structure of the cashew oil modified dicyclopentadiene type phenolic resin estimated from the ¹H-NMR spectrum.

Because the dicyclopentadiene groups that form the main skeleton of the dicyclopentadiene type phenolic resin are aliphatic groups with a large molecular weight, this resin has high compatibility with rubber, which is also aliphatic, in comparison with ordinary phenolic resins. Moreover, if dicyclopentadiene type phenolic resin is modified with aliphatic cashew oil, the proportion of aliphatic groups increases further, resulting in a further increase in compatibility with rubber.

Table 3 shows the results of measurement of the mean particle size of phenolic resins dispersed in natural rubber before vulcanization obtained by SEM observation of the freezing fracture surface of kneaded samples prepared by melt-kneading 15 % of each phenolic resin. The order of the mean particle size of the phenolic resins is: cashew oil modified dicyclopentadiene type phenolic resin < dicyclopentadiene type phe-

Table 3 Mean particle size of phenolic resins in natural rubber

Phenolic resin	Average molecular weight of phenolic resin	Particle size of phenolic resin (μm)
Novolac	4 428	14.1
Dicyclopentadiene type	1 750	8.4
Cashew oil modified dicyclopentadiene type	3 159	6.8

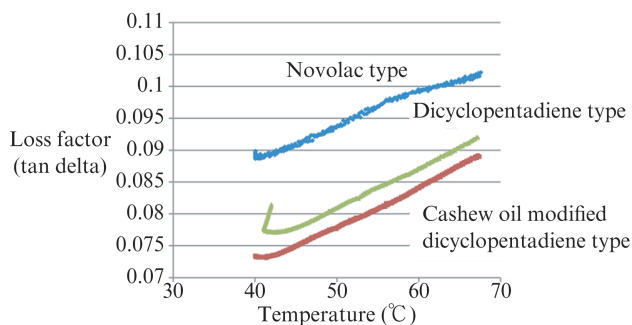


Fig. 8 Tan delta of vulcanized hardened product of natural rubber and 15% phenolic resins

nolic resin < novolac type phenolic resin. These results confirmed that the cashew oil modified dicyclopentadiene type phenolic resin is most easily dispersed and has excellent compatibility with natural rubber.

Figure 8 shows the loss factor of vulcanized hardened products of natural rubber containing 15 % of the respective phenolic resins. Here, 15 % of each phenolic resin was blended in the natural rubber before vulcanizing, carbon black, sulfur and a curing catalyst were added, after which the samples were melt-kneaded and rolled to a sheet form with a two-roll mill, and then vulcanized and hardened at 220 °C using a vacuum press.

The loss factors of the vulcanized hardened products at 40 °C to 65 °C were influenced by the type of blended phenolic resin, and increased in the order of: cashew oil modified dicyclopentadiene type phenolic resin < dicyclopentadiene type phenolic resin < novolac phenolic resin. Thus, the hardened rubber containing the blended cashew oil modified dicyclopentadiene type phenolic resin showed the lowest loss factor.

It is known that the fuel economy of automobiles is affected by the loss factor of the tire material. Tire rolling resistance, which is related to fuel economy, is generated because part of the power transmitted to the tires is used as energy for tire deformation (hysteresis), and that energy is dissipated by heat generation. As the loss factor ($\tan \delta$) of the dynamic viscoelasticity of the material becomes smaller, the proportion of power consumed by heat generation decreases, and as a result, rolling resistance decreases and fuel economy performance improves¹⁰. Because the cashew oil modified dicyclopentadiene type phenolic resin developed by JFE Chemical is easily mixed in natural rubber and the loss factor of the blended rubber product is small, this is an excellent phenolic resin for use as an additive for automobile tires which contributes to improved fuel economy.

Sections 2.2 to 2.4 introduced the features and applications of the developed products based on this company's dicyclopentadiene type phenolic resin. JFE

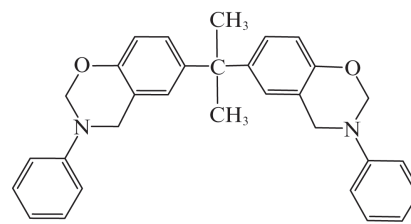


Fig. 9 Bisphenol A type benzoxazine

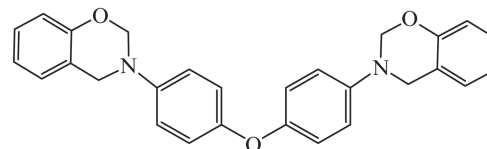


Fig. 10 Oxydianiline type benzoxazine

Chemical's dicyclopentadiene type phenolic resins (J-DPP Series) includes three grades with different softening points, J-DPP-85 (softening point: 85 °C), J-DPP-95 (softening point: 95 °C) and J-DPP-115 (softening point: 115 °C), making it possible to supply the optimum product for the customer's application.

2.5 Benzoxazine

Benzoxazine is a general term for compounds which have a benzene ring and an oxazine ring. When heated to 180 °C or higher, self-curing occurs without using a hardener or catalyst, and the compound changes to a hard cured product (benzoxazine resin) with high heat resistance¹². Since addition of a hardener or catalyst is not necessary, benzoxazine resin has high purity and also possesses excellent flame retardance. Although benzoxazine is not a phenolic resin in the strict sense, it will be discussed in this chapter because the phenolic hydroxy group is utilized in the curing process and the resin displays reactivity with epoxy resins similar to that of the phenolic resins.

Benzoxazines were produced industrially from an early date, and include a type which is synthesized from aniline, bisphenol and formaldehyde and has bisphenol A or bisphenol F in the skeleton (**Fig. 9**). However, the thermal decomposition temperature of this compound was not necessarily high because it contains a large number of easily-oxidized aliphatic C-H bonds. As a further problem, since aniline was used as a feedstock, formation of toxic aniline by thermal decomposition was also a possibility.

In contrast to the conventional benzoxazine, JFE Chemical developed a benzoxazine (**Fig. 10**) using oxydianiline, which is used in polyimides. Because the developed oxydianiline type benzoxazine consists of an ether linkage bonded to aromatic rings, which have high oxidation resistance, and the number of aliphatic

Table 4 Glass transition temperature of cured product of benzoxazine

Benzoxazine	Bisphenol A type	Oxydianiline type
Decomposition temperature (°C, 5%weight loss in air)	334	388
Glass transition temperature (°C, DSC)	155	170

C-H bonds is smaller than in other benzoxazines, the thermal decomposition temperature of cured products is high, and durability and reliability when used under high temperature environments are improved. As a guideline for the thermal decomposition temperature, comparing the 5 % weight loss temperature of cured products in air, the thermal decomposition temperature of the developed oxydianiline type benzoxazine is 388 °C, which is more than 50 °C higher than the 334 °C of the conventional bisphenol A type. In addition, the glass transition temperature is also 15 °C higher than that of the bisphenol A type (Table 4). The oxydianiline type also has the advantage that substantially no aniline is formed by thermal decomposition, as aniline is not used as a feedstock.

One additional feature of the oxydianiline type is the excellent dielectric properties of cured products. In comparison with cured products of epoxy resin and phenolic resin, which are general circuit board materials, the dielectric constant and dielectric tangent of the oxydianiline type are 3/5 and 1/5 of the conventional levels, respectively (Fig. 5). Because of these properties, the oxydianiline type benzoxazine is used as the resin for the circuit boards of electronic equipment in which low dielectric properties are a priority.

In benzoxazine, when the phenolic hydroxy group is used in the process of heating and self-curing, it also acts as a hardener for high heat-resistance epoxy resins and bismaleimide resins. Due to this synergistic effect, cured products obtained by reaction with a high heat-resistance resin have higher heat resistance and a higher thermal decomposition temperature than the cured products using simple benzoxazine.

Considering the excellent heat deterioration resistance and electrical properties of the oxydianiline type benzoxazine, promising applications for this resin in the EV and hybrid vehicle field include sealing materials for the above-mentioned next-generation (SiC) power devices and their peripheral resin parts, and semiconductor sealing materials and board resins for engine control units (ECUs), which are used for long periods in the high temperature environment of the engine compartment.

This product has also been used with satisfactory results as a binder resin for carbon fiber composite

Table 5 Electrical characteristics of cured benzoxazine and an epoxy resin

Resin	Ortho-cresol novolac epoxy resin	Oxydianiline type benzoxazine
Hardeners	Novolac type phenolic resin	NONE
Relative permittivity (1 GHz)	3.39	2.73
Loss tangent (1 GHz)	0.034	0.007

materials, which are increasingly used as automotive interior and exterior materials from the viewpoint of auto body weight reduction¹³⁾. Cured products using benzoxazine have the high heat resistance, and in comparison with the conventional epoxy resin binders which require a hardener, these products also have the advantage of having no strength defects due to unreacted hardener because a hardener or catalyst is not necessary in the curing reaction.

3. Conclusion

This paper compared the features of JFE Chemical's functional phenolic resins with those of conventional phenolic resins, and introduced applications in the fields of EVs and hybrid vehicles and electronic devices such as smartphones, etc.

In comparison with the conventional phenolic resins, the heat resistance of JFE Chemical's trisphenol methane resin is 35 °C higher, the dielectric properties of the dicyclopentadiene type phenolic resin are 20 % lower, and the heat deterioration resistance of benzoxazine is 54 °C higher. The two developed products also have excellent transparency and compatibility with rubber used in tires.

Taking advantage of these respective properties, JFE Chemical's functional phenolic resins can be used with excellent results as sealing materials for power devices for EVs and hybrid vehicles, circuit board materials of engine control units, circuit board materials for 5G smartphones and other electronic equipment, reinforcing materials for rubber used in tires, and binder resins for carbon reinforced composite materials for automotive interior and exterior applications.

References

- 1) Publication number JP, 2008-184417, A
- 2) Takahashi, A. Next Generation Power Device Module and Polymer Materials. Proceedings of The 26th JIEP Annual Meeting. 2012, p. 28-31.
- 3) Nakamata, Y.; Tachioka, M.; Ichimura, Y. Enhanced Thermal Resistance of Molding Resin Used for All-SiC Modules. *Fuji Denki Giho*. 2016, vol. 89, no. 4, p. 247-250.
- 4) Mizuno, Y. Low Dielectric Constant and Low Dissipation Factor Material for High-Frequency PCBs. *Kobunshi*. 2003, vol. 52, p. 571.

- 5) Nanba, H.; Nishijima, Y.; Kawamura, M.; Tamao, M. Jishikuropetanjienn/Feno-ru Kyoujuugoubutsu no kagakukouzou ni kansuru kenkyuu. Proceedings of the thermosetting plastics symposium Japan. 1988, vol. 38, p. 111–114.
- 6) Ogura, I. Relation between Chemical Structures and Characteristics on Epoxy Resins. DIC Technical Review. 2001, no. 7, p. 1–12.
- 7) Publication number JP, 05–214051, A(1993)
- 8) Publication number JP, 2017–036428, A
- 9) Publication number JP, 2018–188590, A
- 10) Ayuta, A. Phenolic Resin for Reinforcing Rubber. Journal of Network Polymer, Japan. 2012, vol. 33, no. 5, p. 281–288.
- 11) Publication number JP, 2019–196431, A
- 12) Takeichi, T. Recent Development of Polybenzoxazine Aiming for High Performance Network Polymer. Journal of Network Polymer, Japan. 2015, vol. 36, no. 2, p. 96–103
- 13) Publication number JP, 2008–094961, A