Technical Report

Environment Responsive (Phosphorus-containing) Epoxy Resin

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Abstract

Flame retardant epoxy resins are being transitioned from brominated epoxy resins to environmentally responsive phosphorus-containing epoxy resins. Furthermore, in recent years, there has been a growing need for reactive flame retardants due to concerns about additive flame retardants leaching into the environment. We developed a phosphorus-containing epoxy resin suitable for use in rigid printed wiring boards by controlling the type of phosphorus compound and the molecular skeleton and molecular weight of the reacting epoxy resin.

1. Introduction

Printed wiring boards used in electronic and electrical equipment are given flame retardancy to prevent fires. The epoxy resins used for this purpose were given flame retardancy by bromination. Since it was suspected that harmful brominated substances (hydrogen bromide, brominated dioxins, brominated benzofurans, etc.) would be generated under certain combustion conditions, the demand has emerged for halogen-free materials (**Fig. 1**).

Also, when bromination is used to provide flame retardancy, it expresses a radical trapping effect in the gas phase. It generates a lot of smoke, raising concerns that evacuees may be engulfed in the smoke and unable to escape in time.

One method of imparting flame retardancy without using halogens is to introduce phosphorus atoms. Phosphorus atoms produce a glassy char of polyphosphoric acid in the solid phase and block and insulate the gases produced by combustion decomposition, thereby exerting flame retardancy.[1] As shown in the photos of the flame retardancy test of the laminates (**Fig. 2**), when flame retardancy is imparted using phosphorus atoms, smoke generation is suppressed compared to bromine-based systems.

Red phosphorus and other additive phosphorus-based flame retardants exist. Concerns have arisen that they may bleed out or leach from discarded equipment, leading to the pollution of rivers and oceans, and have increased the need for reactive phosphorus-based flame retardants.

2. Main Body

As a method for introducing phosphorus atoms, we focused on 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO),[2] which has active hydrogen bonded directly to the phosphorus atom. We synthesized bifunctional phenolic compounds by reacting DOPO with quinone compounds such as 1,4-benzoquinone (HQ) and 1,4-naphthoquinone (NQ)[3, 4] (**Fig. 3**).

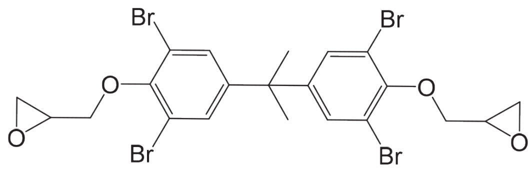

Fig. 1 Brominated epoxy resin

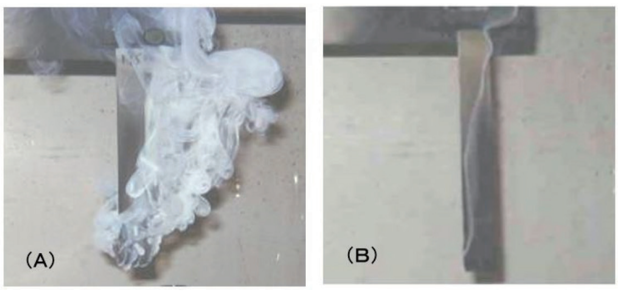

Fig. 2 Photo of flame test of laminate
(A) Brominated epoxy resin, (B) Phosphorus-containing epoxy resin

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By reacting these three types of phosphorus compounds with various epoxy resins, we developed phosphorus-containing epoxy resins that meet the physical properties required for rigid printed wiring boards, such as heat resistance, adhesion to copper foils and glass cloth, and impregnation into glass cloth (reducing the viscosity of the resin).

2.1 Investigation of physical properties depending on the type of phosphorus compound

When DOPO is used as the phosphorus compound, a phosphorus-containing epoxy resin can be obtained by reacting one active hydrogen bonded directly to the phosphorus atom with an epoxy group. Since the epoxy group that reacts with DOPO cannot contribute to the curing reaction, it is necessary to react at least one DOPO with a resin that has three epoxy groups per molecule, leaving two epoxy groups. This results in a phosphorus-containing epoxy resin that can be crosslinked (**Fig. 4**).

On the other hand, DOPO-HQ and DOPO-NQ have two phenolic hydroxyl groups that react with epoxy groups. Even if they react with difunctional bisphenol-type epoxy resins, which are general-purpose epoxy resins, they produce cross-linkable epoxy resins because there are two epoxy groups at the terminals (**Fig. 5**).

2.1.1 Phosphorus-containing epoxy resin using DOPO

A phosphorus-containing epoxy resin was synthesized by reacting a PNE (phenol novolak epoxy resin) with three or more epoxy groups per molecule with DOPO (**Fig. 6**).[5] By varying the amount of reacted DOPO, we confirmed trends in flame retardancy, heat resistance, and resin viscosity.

In the evaluation of the cured product of glass cloth laminates using dicyandiamide as a curing agent (**Fig. 7**), as the phosphorus content increases, i.e., the amount of reacting DOPO increases, the number of components that do not contribute to curing increases, and the heat resistance and adhesive strength decrease. In addition, the resin viscosity increases, causing problems with glass cloth impregnation.

2.1.2 Phosphorus-containing epoxy resins using DOPO-HQ and DOPO-NQ

A liquid bisphenol F epoxy resin (BPF-E) was reacted with DOPO-HQ or DOPO-NQ as a difunctional epoxy resin, and the cured products were evaluated in the same manner as described in Section 2.1.1.[6]

The heat resistance was improved when DOPO-NQ was used compared to DOPO-HQ. This improvement is thought to be due to the rigid naphthalene structure of DOPO-NQ (**Table 1**).

On the other hand, the adhesive strength was sufficiently high.

We also evaluated the PNE (used as described in Section 2.1.1 as multifunctional epoxy resins) and difunctional phosphorus-containing phenol. However, we found that reacting with phosphorus compounds to the extent that flame retardancy could be imparted resulted in an increase in viscosity, which caused problems with the

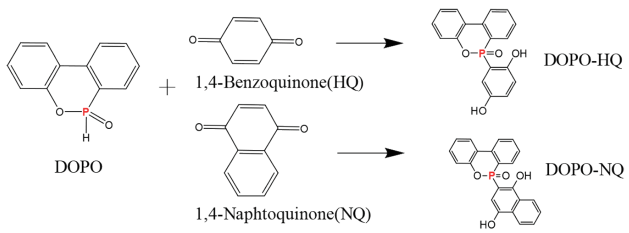

Fig. 3 Reaction between DOPO and quinone compounds

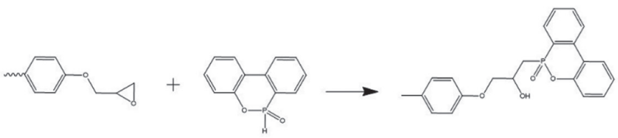

Fig. 4 Reaction of epoxy group and DOPO

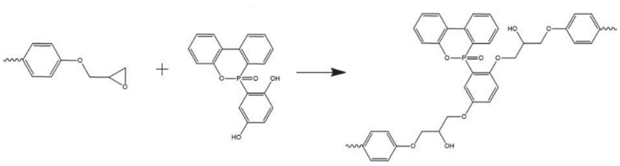

Fig. 5 Reaction of epoxy group and DOPO-HQ

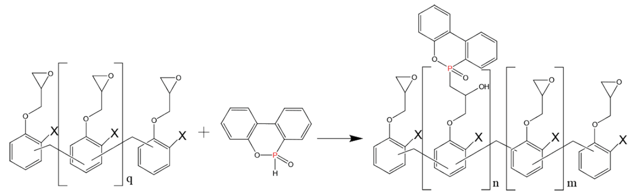

Fig. 6 Reaction of novolac type epoxy resin and DOPO
If X is H, phenol novolak epoxy resin (PNE). If X is CH_3, cresol novolak epoxy resin.

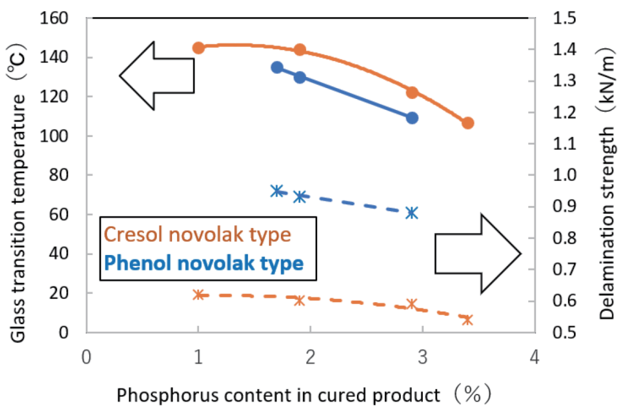

Fig. 7 Relationship between heat resistance and adhesive strength due to DOPO modification

Table 1 Reaction of bifunctional epoxy resin and bifunctional phosphorus-containing phenol compound

Epoxy resins	BPF type epoxy resins	
Phosphorus-containing phenol	DOPO-HQ	DOPO-NQ
Phosphorus content of epoxy resin (%)	3.0	3.0
Glass transition temperature (°C)	109	139
Copper foil peel strength (kN/m)	1.9	1.8
Between layers peel strength (kN/m)	2.2	1.6

glass cloth impregnation.

2.2 Phosphorus-containing epoxy resins using DOPO and DOPO-NQ in combination

We confirmed that the reaction of phosphorus compounds with epoxy resins provides flame retardancy, heat resistance, and adhesive strength. However, the glass cloth impregnation deteriorates as the phosphorus content increases. There is a limit to how much viscosity can be maintained for use.

Therefore, we used DOPO and DOPO-NQ, which have a high phosphorus content of 14.2%, in combination with the PNE used as described in Section 2.1.1 to reduce the resin viscosity (**Table 2**).

The phosphorus content can be increased while maintaining the resin viscosity, but as the DOPO ratio increases, a decrease in the glass transition temperature and adhesive strength is observed.

The combined use of DOPO and DOPO-NQ reduces the resin viscosity. BPF-E, a bifunctional epoxy resin, can also be used to reduce the resin viscosity. This method would enable us to reduce the amount of DOPO used and further increase the amount of DOPO-NQ, a bifunctional phenol, which we thought would improve the adhesive strength.

By using BPF-E in combination, the adhesive strength was improved, while the glass transition temperature gradually decreased (**Fig. 8**).

As the amount of difunctional epoxy resin increases, the reaction with DOPO also produces monofunctional epoxy resins and components that do not contain epoxy groups. This reaction is thought to lead to a decrease in the glass transition temperature.

Using both PNE and BPF-E as epoxy resins, using DOPO and DOPO-NQ as phosphorus compounds, and balancing these components, we succeeded in obtaining a phosphorus-containing epoxy resin for rigid substrates. The phosphorus-containing epoxy resin satisfies the resin viscosity, glass transition temperature of the cured product, adhesive strength, and flame retardancy.[7)]

Table 2 Physical properties based on DOPO/DOPO-NQ ratio

DOPO/Phosphorus-containing phenol ratio	17/83	24/76	36/64
Phosphorus content (%)	2.0	2.4	3.0
Epoxy equivalent (g/eq)	308.2	335.0	330.9
Phosphorus-containing epoxy resin (part)	100.00	100.00	100.00
Dicyandiamide (part)	3.41	3.13	3.17
2-ethyl 4-methylimidazole (part)	0.01	0.25	0.10
Glass transition temperature (°C)	139.9	136.3	127.6
Copper foil peel strength (kN/m)	1.4	1.4	1.3
Between layers peel strength (kN/m)	0.9	0.9	0.9
Flame retardant (UL-94)	V-0	V-0	V-0

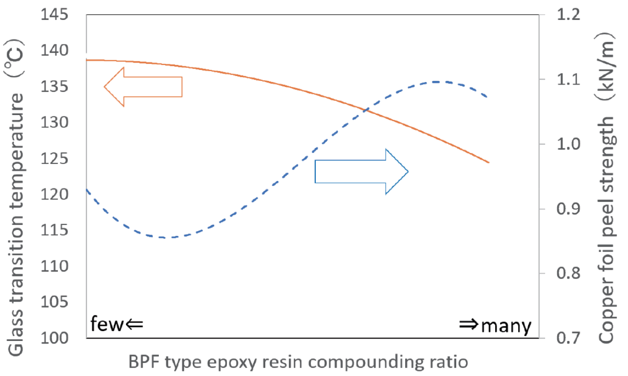

Fig. 8 Relationship between amount of BPF type epoxy resin used, heat resistance, and adhesiveness

2.2.1 Reducing viscosity by changing molecular weight distribution of epoxy resin

When BPF-E is blended with PNE, the viscosity can be reduced by increasing the number of bifunctional components. However, because high molecular weight components are present, even higher molecular weight components are generated through reaction with phosphorus compounds. By using a special PNE with few bifunctional and multifunctional components, it was difficult to generate components that do not contain epoxy groups even with the DOPO reaction and to generate high molecular weight components. We consequently thought that it would be possible to reduce the resin viscosity while improving the heat resistance and adhesive strength.

The reaction was performed by using PNE, which is mainly composed of trimers, and by fixing the DOPO/DOPO-NQ ratio. The solution viscosity of the products dissolved in methyl ethyl ketone (MEK) is shown in **Fig. 9**.

General PNE rapidly increases in viscosity as the phosphorus content exceeds 2%. For PNE with a special molecular weight that is mainly composed of trimers, the viscosity increased gradually. An evaluation similar to that described in Section 2.1.1 was conducted (**Table 3**).

We were able to increase the glass transition temperature while maintaining the flame retardancy and adhesive strength. Also, for applications where a glass transition temperature of around 150°C is acceptable, the phosphorus content can be increased to 2.5%. Because there is a margin for flame retardancy, it is also possible to impart new characteristics by blending other resins.

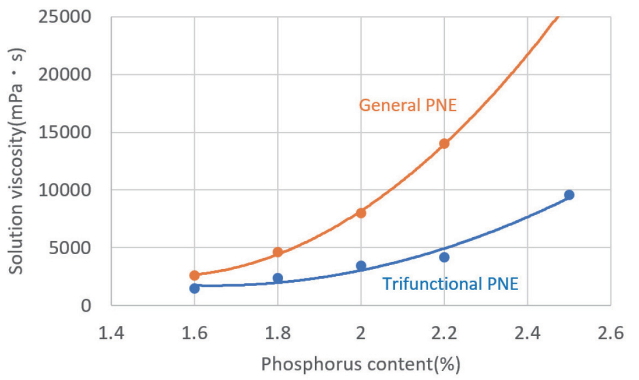

Fig. 9 Relationship between phosphorus content and epoxy resin solution viscosity

Table 3 Physical properties of the reactant of special PN type epoxy resin and DOPO/DOPO-NQ

Phosphorus content (%)	2.0	2.2	2.5
Glass transition temperature (°C)	170	164	159
Copper foil peel strength (kN/m)	1.8	1.7	1.6
Between layers peel strength (kN/m)	1.0	1.0	1.0
Flame retardant (UL-94)	V-0	V-0	V-0

2.3 Study of mass production

We studied an environmentally friendly epoxy resin for mass production. We also investigated waste materials and succeeded in significantly reducing the amount of the cleaning solvent used to clean equipment after the reaction. We believe that environmental friendliness will also be required in manufacturing processes.

2.4 Results and discussion

We used the bifunctional phosphorus-containing phenolic compound obtained by reacting DOPO with a quinone compound as a phosphorus compound. We developed a halogen-free phosphorus-containing flame-retardant epoxy resin for rigid wiring boards by optimizing the skeleton and molecular weight distribution of the epoxy resin that reacts with these compounds. The resin obtained had properties equal to or better than those of the brominated epoxy resin that was previously used. The environmentally friendly epoxy resin helped us to contribute to the production of halogen-free rigid wiring boards.[8)]

3. Conclusions

To address the combustion problem of circuit boards using brominated epoxy resins, we developed a halogen-free flame-retardant epoxy resin using a phosphorus compound. We developed this resin while maintaining the physical properties required for rigid circuit board materials, such as glass cloth impregnation, heat resistance, and adhesiveness, and it also exhibits flame retardancy. In addition, the comparison with the epoxy resins described in this report revealed that conventional brominated epoxy resins reduce the reliability of circuit boards due to bromine dissociation. For this reason, our environmentally friendly epoxy resin has been increasingly used in applications requiring long-term reliability, such as in-vehicle circuit boards.

On the other hand, the need for circuit boards is becoming stronger due to the demand for high-speed communication applications. Such circuit boards are required to have a low dielectric loss tangent as well as halogen-free flame retardancy. The Research & Development Division of Nippon Steel Chemical & Material Co., Ltd. is rigorously working to address this issue.

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