

Development of High Thermal Conductive Epoxy Resin

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Abstract

There have been many reported cases of highly thermally conductive epoxy resins with liquid crystalline epoxy resins with a mesogen backbone; however, due to their strong crystallinity, there have been problems with compatibility and solvent solubility. In this report, we introduce epoxy resins that exhibit high thermal conductivity in a non-mesogen backbone and properties of cured products. In particular, herein we introduce the effect on thermal conductivity due to the curing conditions of a crystalline cured product mainly with a two-dimensional structure, and the effect on the crystalline cured product when a cross-linked structure is introduced, as well as a multifunctional epoxy resin (BDP-E) having a novel biphenyl structure that can be expected to have high thermal conductivity, high T_g , and pyrolytic stability.

1. Introduction

Epoxy resins are widely used industrially because of their excellent heat resistance, moisture resistance, and mechanical and electrical properties. On the other hand, as the required performance properties become increasingly sophisticated, particularly in electrical and electronic applications, greater demand is being placed on the development of highly functional epoxy resins with excellent heat resistance, moisture resistance, and mechanical properties.¹⁾

One of the reasons for this is the advancement of power semiconductors with low power loss, mainly in the in-vehicle field and in relation to the reduction of CO₂ emissions amid growing interest in environmental issues. The encapsulation materials to protect power semiconductors and the substrate materials to mount semiconductor packages are required to have improved functions, such as moisture resistance, heat resistance, toughness, and low thermal expansion.²⁾ In addition, improved properties such as high thermal decomposition stability and high thermal conductivity are also required to support high-temperature operation.

There have been attempts to control the higher-order structure as a method for improving the functionality of epoxy resins. There have been many research examples on liquid crystalline epoxy resins with mesogenic skeletons.³⁾ However, since these epoxy resins do not show a high degree of crystallinity with a melting point, their heat resistance is largely dependent on the glass transition temperature (T_g). The improvement of properties such as moisture resistance and thermal conductivity has been insufficient.

We have previously demonstrated that crystalline phenoxo resins

and cured products can be obtained when epoxy resins with specific structures and curing agents are used.⁴⁻⁶⁾ Crystalline cured products with such melting points (T_m) can ensure heat resistance corresponding to T_m , which is a temperature higher than T_g , and their high crystallinity has been shown to be effective in improving properties such as low thermal expansion, high moisture resistance, and high thermal conductivity. Furthermore, the crystallization of cured products is possible even in systems using epoxy resins that do not have a rigid mesogen skeleton. It is expected that compatibility with curing agents and solvent solubility can be ensured in the preparation of epoxy resin compositions.

In this report, we describe non-mesogenic high thermal conductive resins, including crystalline cured products with mainly two-dimensional structures, crystalline cured products with crosslinked structures, and multifunctional high thermal conductive resins with excellent heat resistance.

2. Crystalline Cured Products with Two-dimensional Structure

2.1 Preparation of diphenyl ether-based cured products

An epoxy resin composition was prepared using 4,4'-diglycidyl ether (DGDE) as an epoxy resin with a non-mesogenic diphenyl ether structure, 4,4'-dihydroxydiphenyl ether (DHDE) as a curing agent, and triphenylphosphine (TPP) as a curing accelerator. The resin was molded at 130°C and post-cured at 170°C into a crystalline cured product (Fig. 1).

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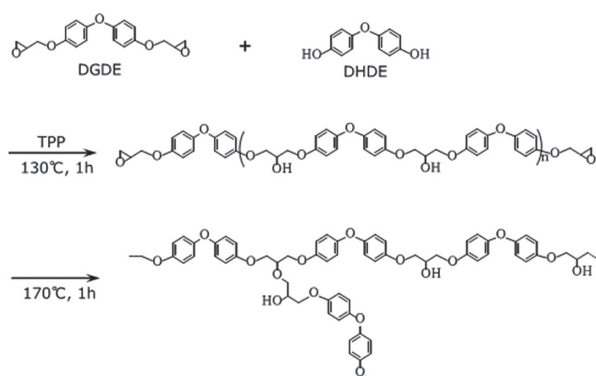


Fig. 1 Polymerization of DGDE/DHDE

2.2 Physical properties of diphenyl ether-based cured products

The cured product was obtained as a yellow-white solid material with no optical transparency. **Figure 2** shows polarizing micrographs of the cured product in the curing process. The epoxy resin composition was melted at around 90°C into an isotropic liquid. The formation of spherulites was confirmed as the temperature increased. The spherulites grew and coalesced at around 100°C. The entire product crystallized at around 110°C. On the other hand, when the epoxy resin composition was molded at 180°C, a yellow-brown, transparent, amorphous cured product was obtained. Rapid heating to 180°C is considered to have accelerated the crosslinking reaction in a random molecular state and inhibited the orientation of the molecular chains.

Figure 3 shows the differential scanning calorimetry (DSC) thermograms of the cured products. The crystalline cured product showed a sharp endothermic peak of 185.6°C in association with the melting of the crystals. On the other hand, the amorphous cured product showed only a T_g -based inflection point at 76.6°C and no endothermic peak corresponding to the melting of the crystals.

Figure 4 shows the relationship between the endothermic amount associated with the melting of crystals and the thermal conductivity of samples with adjusted crystallinity. The thermal conductivity was confirmed to improve by increasing the endothermic amount. The crystalline cured product showed values approximately 1.5 times those of the amorphous cured product. Since the endothermic amount is thought to correspond to the crystallinity degree, the high thermal conductivity of the crystalline cured product may be explained as follows: the intermolecular force increased with the crystallization of the molecular chains, reduced the mobility of the molecular chains, and suppressed the scattering of phonons.

3. Crystalline Cured Products with Crosslinked Structure

Next, we describe the effect of a crosslinked structure on the crystallization behavior and physical properties of cured products when the crosslinked structure was introduced to improve the shape stability of the crystalline polymer obtained through the reaction of an epoxy resin with a phenolic compound having a rigid biphenyl structure.

3.1 Preparation of partially crosslinked crystalline cured products

Multifunctional phenol novolac (PN) was used in the reaction system of 4,4'-diglycidyldiphenyl ether (DGDE) and 4,4'-dihydroxybiphenyl (DHBP), as shown in **Fig. 5**. The component materials were weighed out so that epoxy groups and the functional groups in the curing agent became equimolar. They were heated and mixed at 160°C, and 0.6 wt% of triphenylphosphine was added. The mixture was quickly stirred and mixed and then quenched into a resin composition. The resin composition was molded by a compression

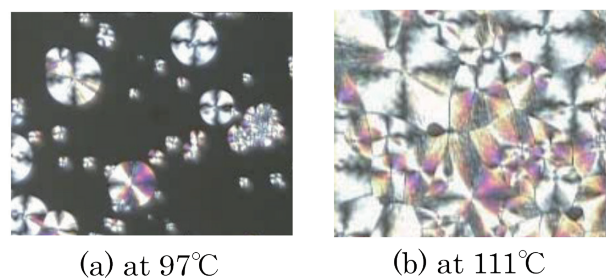


Fig. 2 Polarization micrograph of DGDE/DHDE reaction process

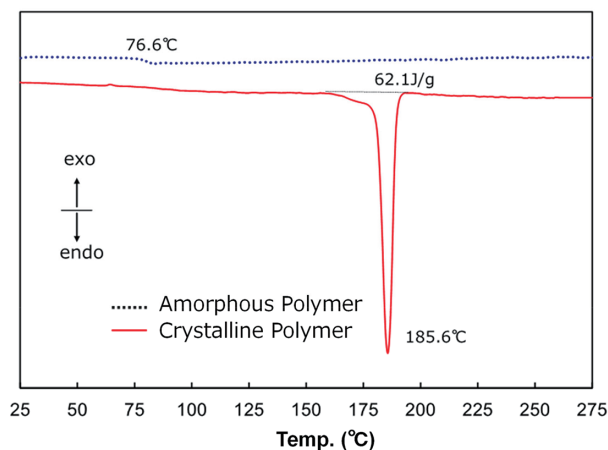


Fig. 3 DSC thermograms of the DGDE/DHDE cured polymers at a heating rate of 10°C/min

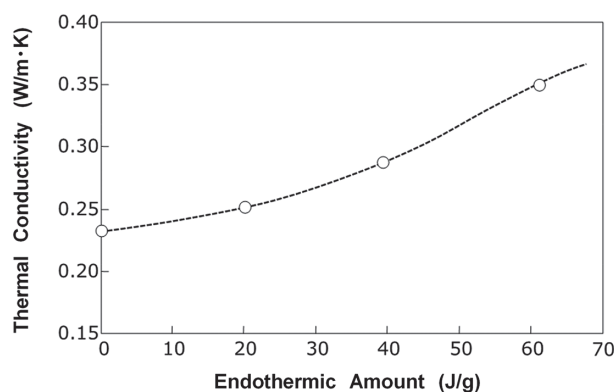


Fig. 4 Thermal conductivity and endothermic amount of crystal melting

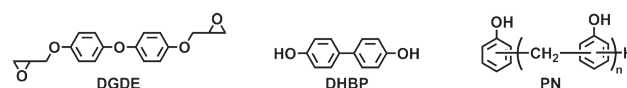


Fig. 5 Structure of epoxy resin and agents

hydroxybiphenyl (DHBP), as shown in **Fig. 5**. The component materials were weighed out so that epoxy groups and the functional groups in the curing agent became equimolar. They were heated and mixed at 160°C, and 0.6 wt% of triphenylphosphine was added. The mixture was quickly stirred and mixed and then quenched into a resin composition. The resin composition was molded by a compression

molding machine at 165°C for 3 min and post-cured in a hot air oven at 175°C for 4 h to prepare test samples.

3.2 Physical properties of partially crosslinked crystalline cured products

The DSC measurement results of the obtained cured products are shown in Fig. 6. The reaction products of DGDE and DHBP were crystalline cured products with no light transparency and with an endothermic peak of 245.6°C. When PN was used together with the curing agent, the endothermic amount associated with the melting of the crystals decreased as the PN content increased. Crystallinity was confirmed to be exhibited until the PN content increased to 60 wt%. This reaction is regarded as a competitive reaction between DHBP and PN with respect to DGDE. It is considered that the reaction between DGDE and DHBP proceeded before the system was fixed by crosslinking with PN and that the orientation of the molecules caused the crystallization. Also, the endothermic peak temperature decreased as the PN content increased. This situation was probably caused by PN inhibiting the growth of molecular chains through the reaction of DGDE and DHBP and decreasing the molecular weight of the molecular chains involved in the crystallization.

Figure 7 shows the relationship of the endothermic amount accompanying the melting of the crystals with the thermal conductivity and moisture absorption in the DSC measurements. It was confirmed that both the thermal conductivity and moisture absorption correlated well with the endothermic amount. The crystalline cured products exhibited high thermal conductivity probably because the crystallization constrained the molecular motion and suppressed the scattering of phonons. The moisture absorption decreased probably because the free space volume was reduced by the cohesive force of the molecular chains arising from the crystallization.

Figure 8 shows the dynamic mechanical analyzer (DMA) thermograms of the cured products. The storage modulus (E') of the crystalline cured products was confirmed to decrease in two stages. Crystalline polymers are generally in a state where crystalline and amorphous regions coexist.⁷⁾ The first decrease is considered to correspond to the T_g at which the amorphous phase transitions from a glassy state to a rubbery state. The second decrease is considered to correspond to the T_m at which the crystalline phase transitions to the amorphous phase due to the melting of the crystals. In addition, the E' at 25°C decreased by increasing the PN content. This condition is probably due to the fact that the increase in the PN content increased the crosslink density, inhibited the packing of the molecular chains, and decreased the E' . On the other hand, the E' at 180°C decreased by increasing the PN content. The reduction in the crystallinity of the cured products may explain this situation. In addition, the T_g remained at 118°C when the PN content ranged from 0 and 30 wt%. When the PN content was 60 wt%, the T_g increased to 131°C while the crystallinity was maintained. At higher PN contents, the T_m could not be confirmed, and the E' decreased in a single step. The crystallinity was presumably inhibited. Also, when the PN content was 100%, the T_g was 140°C. This condition suggests that there is a limit to achieving both high heat resistance and high thermal conductivity with conventional resin designs that are mainly bifunctional.

4. High Heat Resistance and High Thermal Conductivity Resin

We present here the results of our study on multifunctional epoxy resins with rigid structures, aiming to improve heat resistance

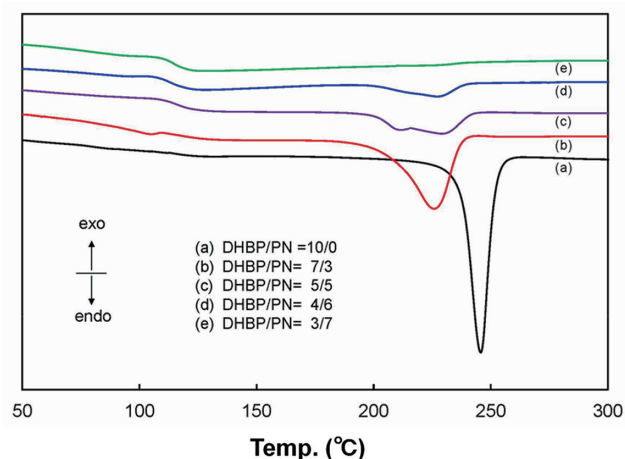


Fig. 6 DSC thermograms of the cured polymers at a heating rate of 10°C/min

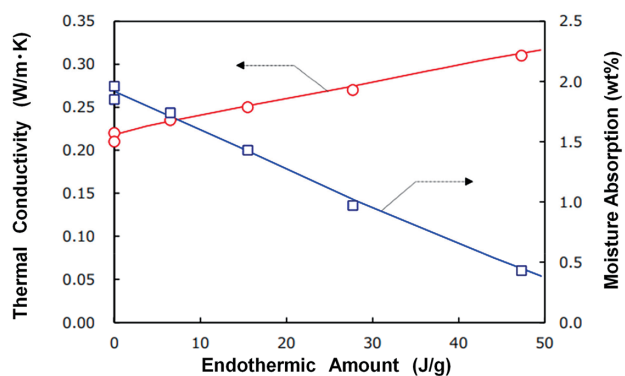


Fig. 7 Thermal conductivity and moisture absorption as a function of the endothermic amount of melting in DSC measurement

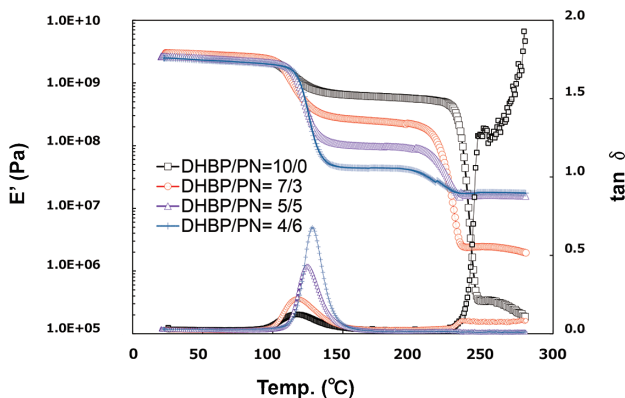


Fig. 8 DMA thermograms of the cured polymers at a heating rate of 2°C/min

further. Approaches to improve thermal conductivity are mainly divided into the suppression of molecular motion by intermolecular interactions and the suppression of molecular motion by intramolecular bonds. The former is thought to be largely due to molecular orientation, i.e., crystallinity, while the latter is considered to be largely due to rigid covalent bonds.

4.1 Preparation of cured resin products containing biphenol structure

Biphenyl aralkyl epoxy resin (BP-E) is an epoxy resin with an introduced rigid structure and it exhibits excellent characteristics such as flame retardancy and reflow soldering heat resistance. However, the introduction of the biphenylene structure is accompanied by a decrease in the crosslink density, which was insufficient in terms of high T_g . Therefore, as a structure capable of controlling a higher introduction ratio of a more rigid structure, Biphenol diphenylnearalkyl epoxy resin (BDP-E) was synthesized by cross-linking biphenol with a biphenylene structure, epoxidized, and cured with phenol novolac. For comparison, BP-E and o-cresol novolac epoxy resin (OCN-E) were also used (Fig. 9).

4.2 Physical properties of cured resin products containing biphenol structure

As shown in Fig. 10, BDP-E cured products were confirmed to have an approximately 20% higher thermal conductivity than that of the BP-E and OCN-E systems used for comparison. The DMA thermograms of the cured products are shown in Fig. 11. The T_g value calculated from the $\tan \delta$ peak temperatures was 211°C, 157°C, and 186°C for the BDP-E, BP-E, and OCN-E cured products, respectively. The superiority of the BDP-E cured products in both thermal conductivity and T_g may be ascribed to the increase in the crosslink density arising from the multifunctional structure and to the suppression of molecular motion arising from the rigidity of the biphenyl structure. The storage modulus of the BDP-E cured products in the rubber state was also higher than that of the other cured products. This result may also be ascribed to the increase in the crosslink density arising from the multifunctional structure.

For long-term thermal stability testing, cured products containing 83 wt% silica fillers were prepared. The change in the flexural strength retention rate of the cured products at 200°C for 1000 h was examined (Fig. 12). Accordingly, the BDP-E cured products showed a flexural strength retention rate 11% higher than that of the BP-E cured products. This is probably because the BDP-E cured products showed a high T_g value above the test temperature and their thermal decomposition was suppressed at 200°C below the T_g as molecular motion was suppressed. On the other hand, the BP-E cured products showed a high weight retention rate but a low flexural strength retention rate. At 200°C, the T_g is exceeded, and the elastic modulus drops significantly, facilitating the formation of foam layers to trap the decomposition products. As a result, the decomposition products do not volatilize, and the apparent weight retention rate remains high. On the other hand, the chemical decomposition itself progresses, so the strength cannot be maintained but decreases.

5. Conclusions

For non-mesogenic high thermal conductivity resins, the thermal conductivity of crystalline cured products mainly composed of a two-dimensional structure can be controlled by the curing conditions. Furthermore, it has been confirmed that the crystal structure can be maintained even when a locally crosslinked structure is introduced for shape stability. These results provide useful insights for controlling the higher-order structure of high thermal conductivity resins. Additionally, the novel multifunctional epoxy resin with a biphenyl structure (BDP-E) has been confirmed to exhibit high thermal conductivity, high T_g , and high thermal decomposition stability. It is expected to be favorably used in the future as a useful epoxy resin for power device applications where its use in a high-tempera-

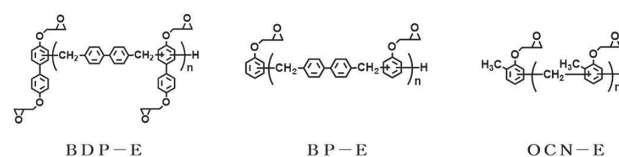


Fig. 9 Structure of epoxy resins

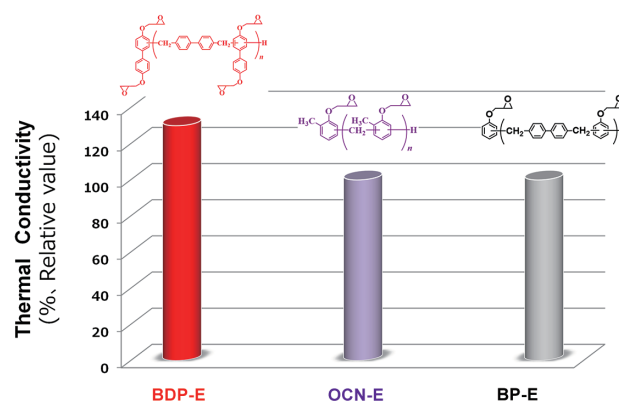


Fig. 10 Relative value of thermal conductivity

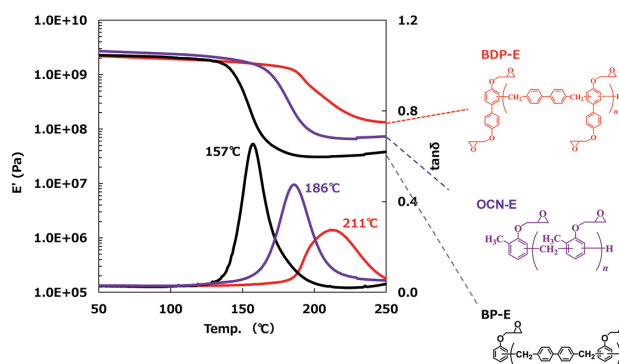


Fig. 11 DMA thermograms of the cured polymers at a heating rate of 4°C/min

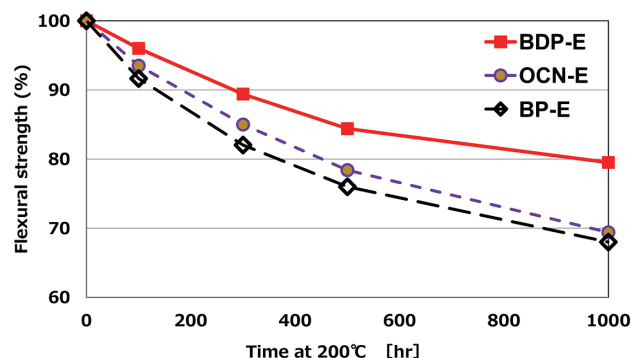


Fig. 12 Flexural strength retention rate of cured resins

ture region of 200°C or higher is anticipated.

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