

New Epoxy-Imide Resins Cured with Bis(hydroxyphthalimide)s

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Synopsis

New epoxy-imide resins were synthesized using *bis*(hydroxyphthalimide)s (BHPIs). Among these resins, that cured with BHPI(DDS), synthesized from 4,4'-diaminodiphenylsulfone, exhibits the best thermal resistance, reaching a $\tan \delta$ maximum temperature of 230°C. This resin also features a tensile lap shear adhesive strength of 320 kgf/cm² when applied to steel test pieces. The cure reaction was followed by infrared spectroscopy and dynamic mechanical analysis. The ring-opening reaction between the phenolic hydroxyl group of BHPI and the epoxy group is observed, and accelerated by a tertiary amine catalyst, triethylamine.

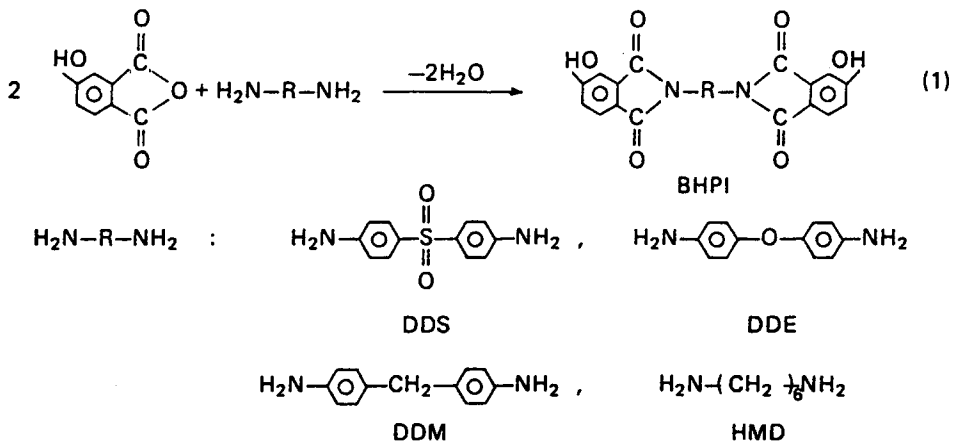
INTRODUCTION

Polyimide has been used widely in the electronics and aerospace fields because of its excellent thermal resistance. It also has a high adhesive strength, when used for adhesive purposes.^{1,2} Polyimide adhesive has two major disadvantages, however, in that it is very expensive, and requires a high cure temperature above 250°C. In an effort to overcome these disadvantages, researchers have been focusing their attention on epoxy-imide resins.^{3,4} However, no one has yet tried to incorporate imide compounds featuring active hydroxyl groups into epoxy-imide resin. We accordingly undertook a study of such a resin, and synthesized new epoxy-imide resins using imide compounds, namely, *bis*(hydroxyphthalimide)s (BHPIs) as epoxy resin curing agents. This paper describes the thermal and mechanical properties of the formed epoxy-imide resins, and outlines the cure reaction.

EXPERIMENTAL

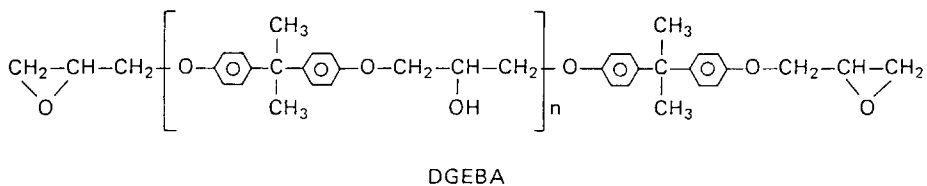
Preparation of Epoxy-Imide Resins

BHPIs were synthesized through the condensation reaction between 4-hydroxyphthalic anhydride and diamines:⁵



Four diamines were used in the reaction: 4,4'-diaminodiphenylsulfone (DDS), 4,4'-diaminodiphenylether (DDE), 4,4'-diaminodiphenylmethane (DDM), and hexamethylenediamine (HMD); and four BHPIs were obtained: BHPI(DDS), BHPI(DDE), BHPI(DDM), and BHPI(HMD). The reaction was conducted in a *m*-cresol and toluene mixture at 130–140°C, with the water generated as a byproduct being azeotropically removed from the reaction system. The melting points of BHPI(DDS), BHPI(DDE), BHPI(DDM), and BHPI(HMD) were 340–342°C, 309–311°C, 317–319°C, and 259–260°C, respectively. The results of elementary analysis for the BHPIs were in good agreement with the calculated values. The difference between the observed and the calculated values fell within 0.3%.⁵

Mixtures of BHPIs and a diglycidylether of bisphenol A (DGEBA), Epikote 828[®] manufactured by Yuka-Shell Corp., were cured. The epoxy value of the DGEBA was 189 g/equivalent.



BHPI and DGEBA were mixed and thoroughly stirred for 90 minutes at 175°C for 90 min. No solvent was used in this process. The precured resin was then cooled and subjected to about 5 Torr to remove air and other volatiles. It was next cured at a prescribed temperature.

BHPI and DGEBA pre-cure mixtures with and without a catalyst, triethylamine (TEA), were also prepared in order to closely follow the cure reaction. A 0.05 mol of TEA was added per mol of the epoxy group in the mixture. The mixing process was conducted at room temperature for both the mixtures with

and without the catalyst in order to prevent the cure reaction from progressing. Free TEA, which was unattached to the reaction system, was removed in the vacuum treatment.

Measurement

Thermal decomposition resistance was evaluated by thermogravimetric analysis (TGA) on a Shimadzu TG-30 Thermal Analyzer. The measurement was taken in an air atmosphere at a heating rate of 10°C/min.

The dynamic mechanical properties were measured in forced vibration on a Toyo Baldwin Rheovibron Dynamic Viscoelastometer (DDV-3-EA). The storage modulus (E') and $\tan \delta$ were recorded as a function of temperature. The measurement conditions were a frequency of 11 Hz, and a heating rate of 1°C/min. Samples were shaped in sheets of 40 × 10 × 1 mm.

The cure reaction was followed by infrared (IR) spectroscopy on a Nicolet MX-1 FT-IR Spectrometer. The precure mixture was dispensed on a KBr plate. It was then cured. The spectrum change was recorded during the cure reaction.

The storage rigidity (G') change in the cure process was also measured in forced torsion on a Rheometrics' Mechanical Spectrometer (RMS-800) in order to follow the cure reaction. The precure resin was inserted into a 2 mm gap between 25 mm diameter aluminum discs. G' was recorded, while the sample was heated at a constant temperature, or in a linearly rising temperature at a heating rate of 2°C/min. The torsional frequency was 10 rad/s, and the applied oscillatory strain was automatically controlled from 0.01 to 100% in the "Auto Strain" mode.

Tensile lap shear adhesive strength was measured at various temperatures on an Instron Universal Testing Instrument (Model TT-CM). Steel test pieces, JIS (Japan Industrial Standard) G 3141-SPCC-SB, were used. The crosshead displacement rate was 10 mm/min. The measurement method was based on JIS 6850.

RESULTS AND DISCUSSION

Properties of Epoxy-Imide Resins

Figure 1 shows the TGA thermograms of epoxy-imide resins. BHPI(DDS) resin exhibits the best thermal resistance with the other resins following in descending order from BHPI(DDE) resin, BHPI(DDM) resin, to BHPI(HMD) resin. All the TGA curves clearly fall in two steps. The decomposition temperatures (PDTs) at each step, determined by the intersections of the tangents to the remaining portions and the falling portions at the significant weight losses in the TGA curves, are very close. The PDTs at the first step are around 380°C, while those at the second step are around 540°C, quite near to those of polyimides. In addition, the height of the second step for BHPI(HMD) resin is much lower than those for the other resins. This result is probably due to the BHPI weight content being lower than those of the others.

The dynamic mechanical properties of the epoxy-imide resins are shown in Figure 2. The mechanical thermal resistance was evaluated using the $\tan \delta$

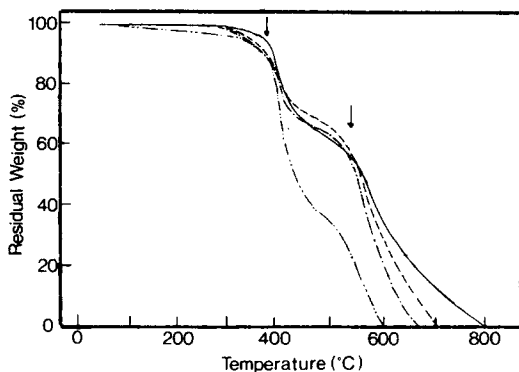


Fig. 1. TGA thermograms of epoxy-imide resins in air; cure conditions: BHPI content ($M_{OH}/epoxy$: molar ratio of phenolic hydroxyl group to epoxy group) = 0.75, cure temperature = 200°C, and cure time = 6 h. (—) BHPI(DDS) resin; (---) BHPI(DDE) resin; (-·-) BHPI(DDM) resin; (····) BHPI(HMD) resin.

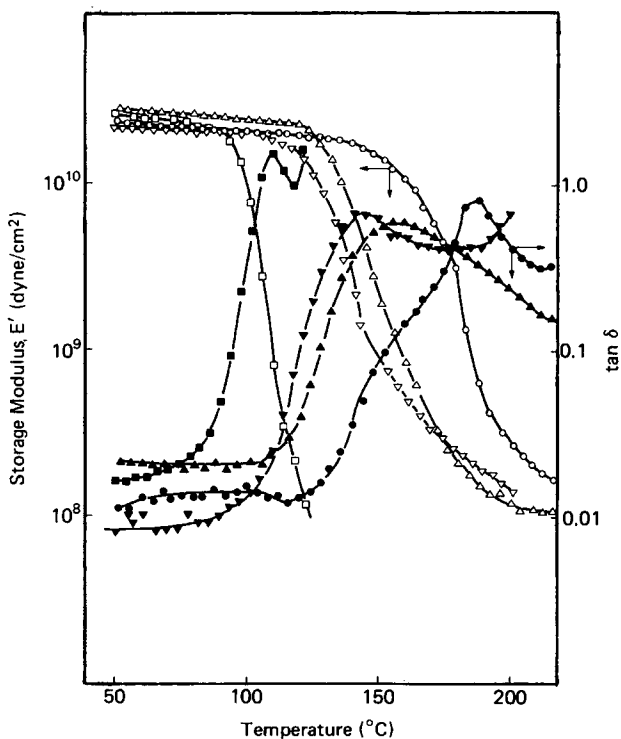


Fig. 2. Dynamic mechanical properties of epoxy-imide resins: \circ \bullet = BHPI(DDS) resin, Δ \blacktriangle = BHPI(DDE) resin, ∇ \blacktriangledown = BHPI(DDM) resin, and \square \blacksquare = BHPI(HMD) resin; cure conditions: $M_{OH}/epoxy$ = 0.75, cure temperature = 200°C, and cure time = 6 h.

maximum temperature (T_{max}). In terms of mechanical thermal resistance, the resins in descending order are BHPI(DDS) resin, BHPI(DDE) resin, BHPI(DDM) resin, and BHPI(HMD) resin. This result indicates that the BHPI structure, or its structural rigidity greatly affects the mechanical properties of these resins. The T_{max} of BHPI(HMD) resin, which has a flexible aliphatic structure in the BHPI part, is much lower than those of the others.

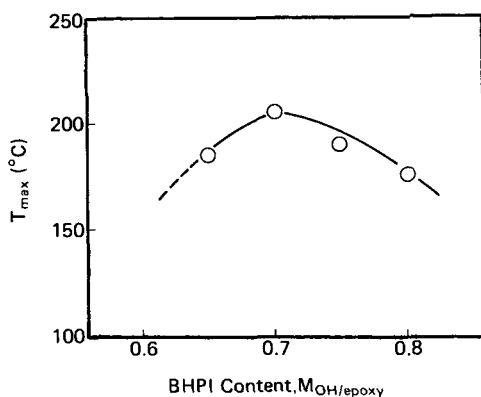


Fig. 3. Relationship between T_{max} and BHPI content for BHPI(DDS) resin; cure conditions: cure temperature = 200°C, and cure time = 6 h.

The polarity of BHPI should also affect the mechanical properties. The high polarity of the sulfone group in BHPI(DDS) is considered to contribute to the noticeably high T_{max} of BHPI(DDS) resin in that it increases the attracting force between polymer chains. Mita pointed out this effect⁶ concerning those polyimides synthesized from DDS, DDE, DDM, and 2,2-bis(3',4'-dicarboxyphenyl)hexafluoropropane dianhydride by Gibbs and Breder.⁷

We next investigated the cure conditions for BHPI(DDS) resin, which showed the best thermal resistance. The relationship between T_{max} and the BHPI content is shown in Figure 3. Here, the BHPI content is expressed by the molar ratio of the phenolic hydroxyl group to the epoxy group ($M_{OH/epoxy}$). The BHPI(DDS) resin shows a maximum T_{max} of 205°C when the $M_{OH/epoxy}$ was 0.7, which is supposed to be the optimum content. On the other hand, when the $M_{OH/epoxy}$ was lower than 0.65, the cured resin was too brittle to handle.

Figure 4 shows the relationship between T_{max} and the cure temperature. BHPI(DDS) resin had a T_{max} of 203°C when the cure temperature was 200°C. The T_{max} reached 230°C when the cure temperature was 220°C, but remained

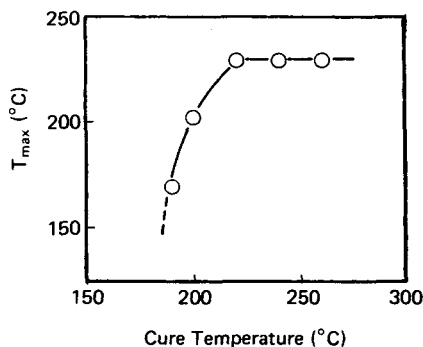


Fig. 4. Relationship between T_{max} and cure temperature for BHPI(DDS) resin; cure conditions: $M_{OH/epoxy}$ = 0.7, and cure time = 3 h.

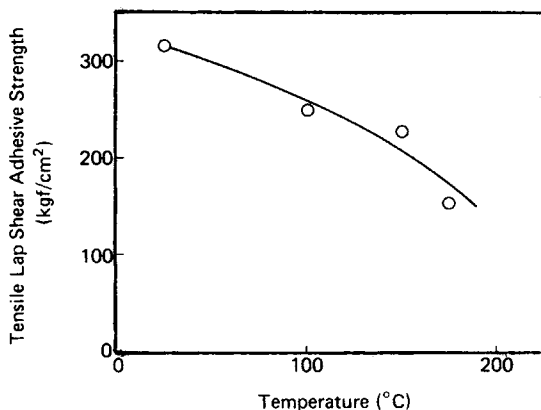


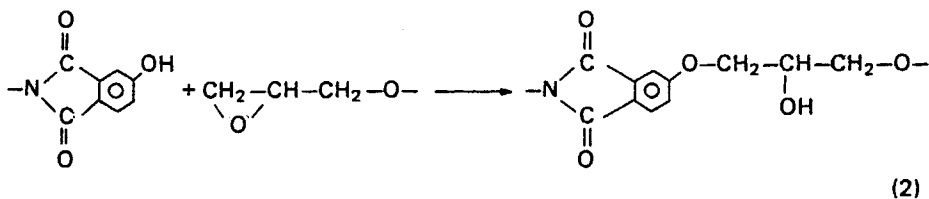
Fig. 5. Tensile lap shear adhesive strength of BHPI(DDS) resin using steel test pieces; cure conditions: $M_{OH/epoxy} = 0.7$, cure temperature = 200°C, and cure time = 6 h.

around 230°C above this cure temperature, implying that the cure reaction was completed. On the other hand, the cured resin was brittle at cure temperatures under 190°C.

The adhesive strength values of BHPI(DDS) versus temperature are shown in Figure 5. BHPI(DDS) clearly exhibits excellent adhesive strength, reaching 320 kgf/cm² at room temperature. Although the adhesive strength gradually decreases with the increase in temperature, this resin still retains an adhesive strength of 150 kgf/cm² at 175°C. The authors believe that this resin is one of the most promising materials for high-temperature adhesive application.

Cure Reaction

The IR spectral change resulting from the cure reaction between BHPI(DDS) and DGEBA is given in Figure 6. The broad absorption peak at 909 cm⁻¹ due to the epoxy group decreases with the progress of the cure reaction. At the same time, the absorption peak at 3400 cm⁻¹ due to the phenolic hydroxyl group shifts to that at 3500 cm⁻¹, and it becomes larger and sharper. The peak wavelength of 3500 cm⁻¹ coincides with that of the alcoholic hydroxyl group in DGEBA. The formation of the alcoholic hydroxyl group is supported by the increase in the peak height around 1100 cm⁻¹. Overall, the cure reaction is thought to progress according to the scheme:



In this scheme, the epoxy group and the phenolic hydroxyl group are consumed, with the alcoholic hydroxyl group, which is similar to that of DGEBA, being subsequently generated.

The dangling alcoholic hydroxyl groups of DGEBA and growing polymer chain have reactivity with the epoxy group. Because this reaction progresses

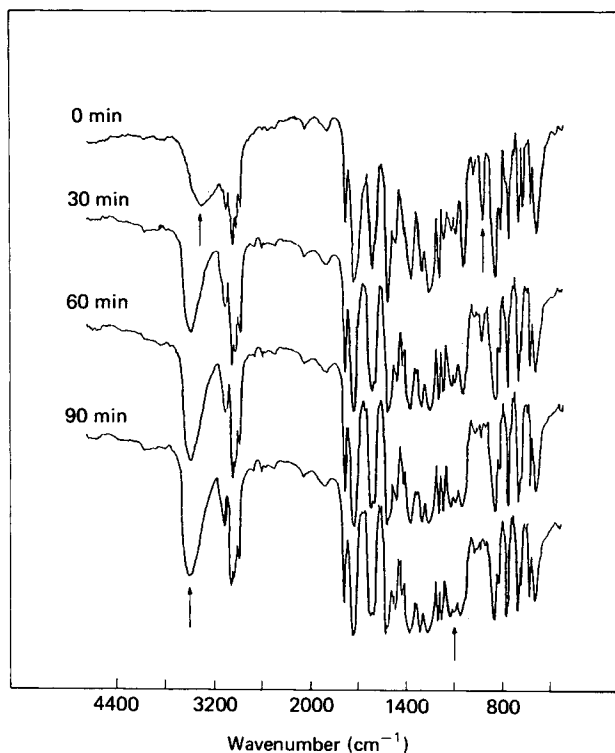


Fig. 6. IR spectrum change caused by cure reaction between BHPI(DDS) and DGEBA at 200°C; $M_{\text{OH/epoxy}} = 0.7$.

at a temperature around 200°C and is accelerated by a phenolic hydroxyl group,⁸ this reaction may take place as a subreaction of the cure reaction. This reaction leads to the polymer chain cross-links in the reaction system studied here. The E' curve shape in Figure 2, in which the rubbery state region is observed, indicates the existence of cross-links, and consequently supports the occurrence of the subreaction. The optimum $M_{\text{OH/epoxy}}$ of 0.7 can be explained by the existence of this subreaction, because excess epoxy group is necessary for this subreaction.

Such a reaction as Scheme (2) is known to be accelerated by base catalysts like tertiary amines.⁹ We therefore investigated the reaction system containing the catalyst, TEA. The G' changes caused by the cure reactions with and without the catalyst are compared in Figure 7.* First, the G' 's gradually fall with the increase in temperature due to the decrease in viscosity. Gel is then formed and G' begins to rise around 240°C in the reaction system without the catalyst, while it begins to rise around 140°C in the reaction system containing the catalyst. These results indicate that TEA highly accelerates the cure reaction. The reaction system containing the catalyst was also followed by IR analysis. The result obtained was almost the same as that of the system without the catalyst, except that the reaction was faster. In other words, no

*The G' curves could not be measured up to plateau regions, because the "Auto Strain" mechanism could not follow the sudden G' changes in the rising portions and became the "overload" state.

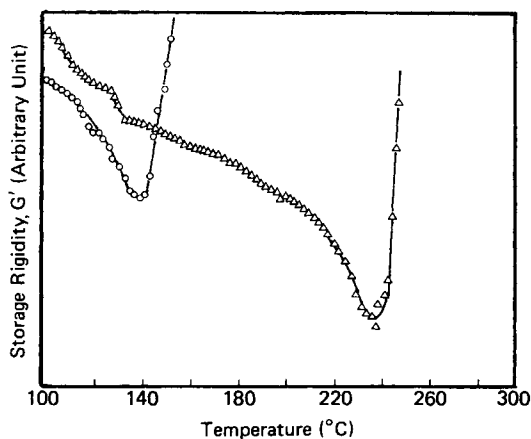


Fig. 7. Dynamic storage rigidity (G') change versus temperature in cure reaction between BHPI(DDS) and DGEBA: ○ = with catalyst, and △ = without catalyst; $M_{OH/epoxy} = 0.7$.

cleavage of the imide ring, or formation of amide and carboxyl groups was observed, which is also accelerated by a base catalyst like TEA. This result excludes the possibility that the epoxy group might react with the amide or the carboxyl groups generated from the imide ring cleavage.

As stated, TEA was effective in terms of catalysis. The formed resin was brittle, however, even when it was cured at a high temperature for a long enough cure time, for example, at 220°C for 6 h. Although the data obtained are insufficient to analyze this result, the authors believe that the selective catalysis of tertiary amine,¹⁰ which preferentially accelerates the reaction between the end groups, phenolic hydroxyl group, and epoxy group, must play an important role in leading to the lack of cross-links. The viscosity of the reaction system must also be an important factor. The reaction system with the TEA catalyst shows the higher minimum G' value. This reaction system is thought to become stiff before an optimum fluid state is obtained. Since the fluid state is concerned with the molecular motion and consequently governs the possibility of reactive groups meeting each other, the reaction must be restricted in the reaction system with the catalyst. As stated thus far, TEA is not a good catalyst in terms of affording mechanical toughness to the cured resin. The authors believe that a tertiary amine catalyst can be useful, however, if it is applied to a reaction system between a multifunctional epoxy resin and a BHPI, and if the cure condition can be adequately controlled. We will be investigating such a reaction system in the near future.

Figure 8 shows the G' change resulting from the cure reaction between BHPI(DDS) and DGEBA at a constant temperature of 200°C. Clearly, G' initially falls as the time proceeds, which is also due to the decrease in viscosity. It is evident from the IR result, however, that the cure reaction proceeds in the falling portion of the G' curve (see the IR spectrum at the cure time of 30 min in Fig. 6). The prepolymer then becomes stiff with the progress of the reaction and G' begins to increase at a cure time of 60 min. Until this time, the absorption peak at 909 cm^{-1} due to the epoxy group has decreased to a very small value in the IR spectrum (Fig. 6), which means the cure reaction has progressed considerably. Furthermore, this peak almost

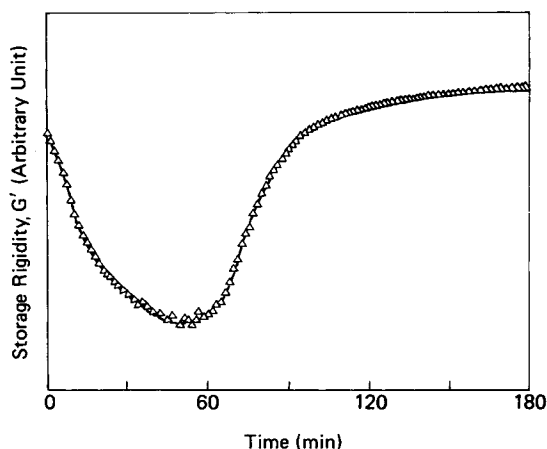


Fig. 8. Dynamic storage rigidity (G') change versus time in cure reaction between BHPI(DDS) and DGEBA; $M_{OH/epoxy} = 0.7$, and cure temperature = 200°C.

disappears at the cure time of 90 min, when the G' value approaches the plateau region.

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