Synthesis of a Bifunctional Epoxy Monomer Containing Anthracene Moiety and Properties of Its Cured Polymer with Phenol Novolac

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Received 2 September 1998; accepted 23 October 1998

ABSTRACT: A new type of epoxy resin containing anthracene moiety in the backbone was synthesized and was confirmed by elemental analysis, infrared spectroscopy, and ¹H nuclear magnetic resonance spectroscopy. Thermal properties of its cured polymer with phenol novolac were examined by thermomechanical, dynamic mechanical, and thermogravimetric analyses. The cured polymer with phenol novolac showed higher glass transition temperature (T_g), lower thermal expansion, lower moisture absorption, and higher anaerobic char yield at 700°C than a cured polymer having a phenylene group in place of anthracene moiety. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 72: 953–959, 1999

Key words: epoxy resin; anthracene derivative; thermal properties

INTRODUCTION

Epoxy resins are of great importance for a number of applications, including surface coatings, adhesives, structural composites, printed circuit boards, microelectronic encapsulation, and insulted materials for electronic devices,¹⁻² because of their good heat and chemical resistance and superior mechanical and electrical properties, in addition to their excellent processabilities. However, the conventional epoxy resins are inefficient to satisfy required properties in the field of advanced materials. For example, the encapsulating resin must comply with strict requirements, which arise from a larger chip size, a higher density of devices, and surface mounting technol-

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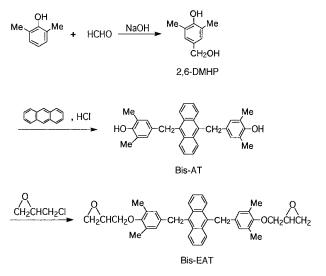
Journal of Applied Polymer Science, Vol. 72, 953-959 (1999)

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ogy.³⁻⁴ These trends require development of highperformance epoxy resins, which have higher thermal and moisture resistance and lower thermal expansion.

It has been reported that T_g and moisture absorption increase as crosslinking density increases in the *o*-cresol novolac epoxy resin system.⁵ For the conventional resin system, a trade off exists between T_g and moisture absorption. Modifications of the backbone of epoxy resins have been recently paid much attention in attempts to enhance thermal and physical properties.⁶ We have reported that naphthalene-based epoxy resins exhibit lower moisture absorption, higher T_g , and lower thermal expansion than the conventional epoxy resins based on their condensed poly-nuclear aromatic structure.⁷

In this article, we wish to report the introduction of an anthracene moiety into the resin backbone in order to examine the effect of condensed



Scheme 1 Synthesis of Bis-EAT.

tricyclic aromatic structure. Montaudo et al. have reported on Friedel–Crafts resin having anthracene moiety in the resin backbone,⁸ and few studies have been reported about anthracene containing epoxy resin. A new type of epoxy resin containing anthracene moiety in the backbone was synthesized, and the thermal properties of the cured polymer obtained from the new epoxy resin and phenol novolac were compared with those from an epoxy resin having phenylene group.

RESULTS AND DISCUSSION

Synthesis of Anthracene Containing Epoxy Resin

The new anthracene containing epoxy resin, 9,10bis[3,5-dimethyl-4-(2,3-epoxypropyloxy)benzyl]anthracene (Bis-EAT), was prepared by the following three steps. Syntheses of 2,6-dimethyl-4-hydroxymethylphenol (DMHP), 9,10-bis(3,5dimethyl-4-hydroxybenzyl)anthracene (Bis-AT), and epoxydation of Bis-AT were carried out, as shown in Scheme 1. The structure of Bis-EAT was confirmed by elemental analysis (EA), infrared spectroscopy (IR), and ¹H nuclear magnetic resonance (¹H-NMR) spectroscopy.

DMHP was obtained by the reaction of 2,6dimethylphenol with formaldehyde in aqueous sodium hydroxide at lower temperature (25°C) in a 62.0% yield. Although Adler et al. have already synthesized DMHP in the same manner, its structure was comfirmed by only the melting point.⁹

Bis-AT was obtained as a yellowish powder by electrophlic substitution reaction of DMHP with anthracene in chlorobenzene in 51.8% yield. As Bis-AT showed poor solubility in chlorobenzene, it was isolated from the reaction mixture during the reaction. In the ¹H-NMR spectrum of Bis-AT, all signals corresponding to the proposed structure were observed in N,N-dimethylformamide-d₇. Three singlet signals were observed at 2.08, 4.95, and 6.75 ppm, which were attributable to the methyl protons, the methylene protons, and the protons on phenyl ring, respectively. Further, two kinds of double-doublet peaks corresponding to the anthracene protons were observed at 7.52 and 8.41 ppm. These results might support strongly that the substitution reaction proceeded at 9 and 10 positions on the anthracene ring.

As shown in Figure 1 (IR spectrum of Bis-EAT), the characteristic band of the oxirane ring was observed at 910 cm⁻¹. The ¹H-NMR spectrum in chloroform-d₁ is shown in Figure 2. The same signal pattern as in Bis-AT were observed, except for the signals corresponding to the glycidyl group. Assignments of the chemical shifts are as follows: 2.16 (singlet, methyl protons), 4.92 (singlet, methylene protons between aromatic rings), 6.78 (singlet, phenyl protons), 7.45 (double-doublet, anthracene protons), 8.27 (doubledoublet, anthracene protons), and 2.66–3.96 ppm (multiplet, glycidyl group protons). Its elemental analysis was in good agreement with the calculated values. The epoxy equivalent weight of Bis-EAT was found to be 280 g eq (calcd 279 g eq).

In order to examine the influence of anthracene moiety in the main chain, 1,4-bis[3,5-dimethyl-4-(2,3-epoxypropyloxy)benzyl]benzene (Bis-EBZ) having phenylene group in place of anthracene moiety was synthesized by the following two steps. Syntheses of 1,4-bis(3,5-dimethyl-4-hydroxybenzyl)benzene (Bis-BZ) and its epoxydation were carried out according to Scheme 2.

The ¹H-NMR spectrum of Bis-EBZ in acetone-d₆ gave four singlet signals. Assignments of the chemical shifts are as follows: 2.19 (methyl protons), 3.78 (methylene protons), 6.86 (phenyl protons on phenol ring), 7.11 (phenyl protons on benzene ring), and 2.62–4.03 ppm (glycidyl group protons). In the IR spectrum of Bis-EBZ, the characteristic band of the oxirane ring was observed at 914 cm⁻¹. Elemental analyses were in good agreement with the calculated values. The epoxy equivalent weight of Bis-EBZ was found to be 232 g eq (calcd 229 g eq).

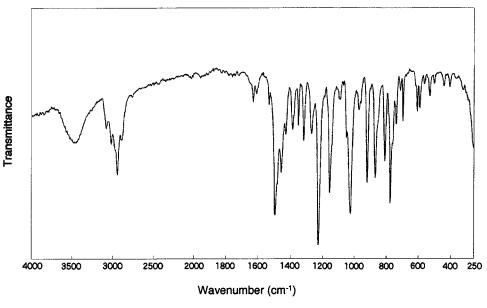


Figure 1 IR spectrum of Bis-EAT.

Properties of Cured Polymers

The results of thermomechanical analyses (TMA) are summarized in Table I. The inflection point of thermal expansion was defined as $T_{g\text{-TMA}}$. Although the cured polymer obtained from Bis-EAT (Bis-EAT polymer) containing anthracene moiety might be considered to have a lower crosslinking density than that of Bis-EBZ (Bis-EBZ polymer),

Bis-EAT polymer showed higher $T_{g\text{-}TMA}$ than that of Bis-EBZ polymer. Figure 3 shows the spectrum of dynamic mechanical analyses (DMA), and their results are summarized in Table II. The peak temperature of tan δ was taken as $T_{g\text{-}DMA}$. The DMA results indicated that Bis-EAT polymer had higher $T_{g\text{-}DMA}$ than that of Bis-EBZ polymer and showed that Bis-EAT polymer gave a lower

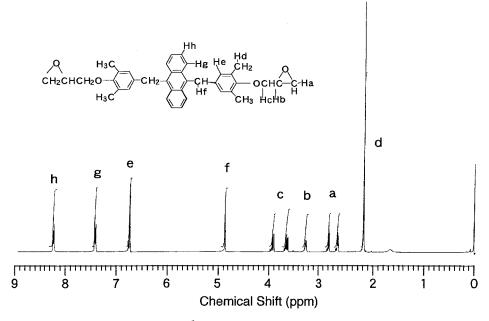
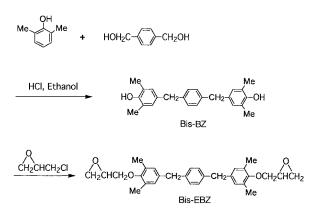


Figure 2 ¹H-NMR spectrum of Bis-EAT.



Scheme 2 Synthesis of Bis-EBZ.

crosslinking density, which might be supported by the lower storage modulus (E') in the rubbery region. In the Bis-EAT polymer, the bulkiness of the 9,10-anthrylene skeleton in the main chain may restrict the rotation of the polymer main chain. And the condensed polynuclear aromatic structure of anthracene can force the thermal movement of the polymer backbone. Incorporation of the 9,10-anthrylene group into the main chain may cause to enhance T_g of the cured polymer obtained from Bis-EAT.

Furthermore, the TMA results may show that Bis-EAT polymer have the smaller coefficients of linear thermal expansion (CTE) in the glassy region and the rubbery region, compared with Bis-EBZ polymer. Especially, the distinctive smaller CTE of $12.7 \times 10^{-5} \text{ °C}^{-1}$ was observed in the rubbery region. We have reported the thermal behaviors in the cured polymers from the naphthalene-based epoxy resins, in which it was showed that the CTEs of the naphthalene-based epoxy resins were in the range of $14.5-17.5 \times 10^{-5} \text{ °C}^{-1}$ in the rubbery regions.¹⁰ The smaller CTEs of the naphthalene-based epoxy resins have been explained in terms of their condensed polynuclear aromatic structures. As a CTE in rub-

Table IThermomechanical Analysis of theCured Polymers

Epoxy Resin	$T_{g\text{-TMA}}_{(°\mathrm{C})}$	$CTE^{a} (\times 10^{-5}, °C^{-1})$	
		Glassy Region	Rubbery Region
Bis-EAT Bis-EBZ	$\begin{array}{c} 151 \\ 135 \end{array}$	5.8 6.2	12.7 17.4

^a Coefficient of linear thermal expansion.

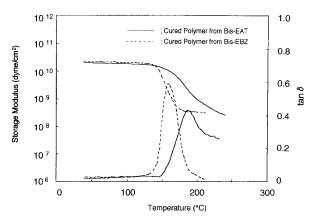


Figure 3 DMA results of the cured polymers from Bis-EAT and Bis-EBZ.

bery region is thought to correspond to micro-Brownian motion of the main chain released above T_g , it seemed that the characteristic small CTE in Bis-EAT polymer depended on the restricted molecular mobility arising from the condensed polynuclear aromatic structure of anthracene in the main chain.

The thermal stability of the cured polymers were compared by the temperature of 10% weight loss and percentage of char yield at 700°C in thermogravimetric analyses (TGA). The TGA curves are shown in Figure 4, and the results are summarized in Table III. The anaerobic char yield of Bis-EAT polymer was higher than Bis-EBZ polymer, which might be attributed to the higher aromaticity of Bis-EAT polymer containing anthracene moiety. On the other hand, Bis-EAT polymer showed a slightly lower thermal decomposition temperature than Bis-EBZ polymer, which was presumably due to the looser crosslinking density in Bis-EAT polymer.

The moisture absorption of the cured polymers is shown in Table IV. Bis-EAT polymer gave lower

Table II	Dynamic	Mechanical	Analysis	of the
Cured Po	olymers			

		Storage Modulus (×10 ⁹ , dyn/cm ²)	
Epoxy Resin	$\begin{array}{c}T_{g\text{-DMA}}\\(^{\circ}\mathrm{C})\end{array}$	Glassy Region ^a	Rubbery Region ^b
Bis-EAT Bis-EBZ	187 161	$\begin{array}{c} 19.5\\ 22.1 \end{array}$	$\begin{array}{c} 0.27\\ 0.32\end{array}$

^a Storage modulus at 30°C.

^b Storage modulus at $T_{g-\text{DMA}}$ + 50°C.

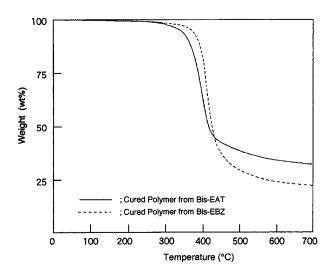


Figure 4 TGA thermograms of the cured polymers from Bis-EAT and Bis-EBZ.

moisture absorption than that of Bis-EBZ. The result seems to depend on the hydrophobic nature of the anthracene moiety and the lower functionality of Bis-EAT arising from an introduction of the large molecular weight of anthracene group. Ogata et al. have reported that the moisture absorption increases as the T_g increases in the cured polymers from o-cresol novolac type epoxy resin and phenol novolac.⁵ This information may mean that it is difficult to decrease the moisture absorption with keeping a higher T_g in the conventional resin systems. However, incorporation of anthracene moiety into epoxy cured polymer was effective for improving moisture resistance and thermal stability.

EXPERIMENTAL

Materials

Anthracene was purified by sublimation. Commercially available 2,6-dimethylphenol, 1,4bishydroxymethyl benzene, acetic acid, ethyl alcohol, ethyl acetate, and 37% formaldehyde were

Table IIIThermogravimetric Analysis of theCured Polymers

Epoxy	Temperature of 10 Wt %	Char Yield
Resin	Weight Loss (°C)	at 700°C (%)
Bis-EAT Bis-EBZ	$\frac{364}{371}$	32 22

 Table IV
 Moisture Absorption of the Cured

 Polymers
 Polymers

Epoxy Resin	Moisture Absorption ^a (Wt %)
Bis-EAT Bis-EBZ	$1.40\\1.65$

^a 133°C; 3 atm; 96 h.

used without further purification. Chlorobenzene and epichlorohydrin were distilled before use. Phenol novolac (Tamanol 758) was obtained from Arakawa Chemical Co. Triphenylphosphine as curing accelerator was used as received from Hokko Chemical Co.

Synthesis of 2,6-Dimethyl-4-hydroxymethylphenol

122.0 g of 2,6-dimethylphenol was dissolved in 100 mL of toluene, and 81.8 g of 37% formaldehyde solution was added. After the solution was cooled to 10°C, 83.3 g of 48% aqueous sodium hydroxide was added dropwise to the solution with stirring below 25°C. The reaction was continued at 25°C for 20 h. The solution was poured into 1500 mL of water and neutralized with aqueous acetic acid solution. The isolate precipitate was collected by filtration and recrystallized from ethyl acetate to obtain DMHP in 62.0% yield (104–106°C mp).

Synthesis of 9,10-Bis(3,5-dimethyl-4hydroxybenzyl)anthracene

50.0 g of DMHP and 29.0 g of anthracene were added to 800 mL of chlorobenzene in a 1000-mL three-necked flask, and the solution was heated at 80°C. To this solution 200 mL of concentrated hydrochloric acid was added dropwise with stirring. The reaction was continued at 80°C for 48 h. The solid product isolated during the reaction was separated by filtration and washed with fresh chlorobenzene, hexane, and water. The obtained Bis-AT was dried at 100°C for 15 h *in vacuo* (51.8% yield; 262–264°C mp).

IR (KBr): 3488, 2916, 1490, 1194, 1144, 1026, 796, 746 cm⁻¹. ¹H-NMR (*N*,*N*-dimethylformamide-d7): δ 2.08 (s, 12H), 4.95 (s, 4H), 6.75 (s, 4H), 7.52 (d, 4H, *J* = 9.90 Hz), 8.18 (s, 2H), 8.41 (d, 4H, *J* = 9.90 Hz) ppm.

Synthesis of 9,10-Bis[3,5-dimethyl-4-(2,3epoxypropyloxy)benzyl]anthracene

35.7 g of Bis-AT was dissolved in 400 mL of epichlorohydrin, and the solution was heated at 70° C to obtain a homogeneous solution; then to this solution 13.3 g of 48% aqueous sodium hydroxide was added dropwise with stirring under reduced pressure (~ 20 kPa) for 4 h. During the reaction, produced water was removed from the solution by azeotropic distillation. The distilled epichlorohydrin was again returned to the solution after separation with water. The greenish-yellow solid product isolated during the reaction was separated by filtration and washed with water. The obtained Bis-EAT was dried at 80°C for 15 h *in vacuo* [95.4% yield; 245–250°C mp; 280 g eq epoxy eq (279 g eq calcd)].

IR (KBr): 2920, 1486, 1216, 1144, 1014, 910, 802, 766 cm⁻¹. ¹H-NMR (chloroform-d₁): δ 2.16 (s, 12H), 2.66 (dd, 2H, J = 2.44, 2.69, 4.88, and 5.13 Hz), 2.85 (dd, 2H, J = 4.39 and 4.88 Hz), 3.31 (m, 2H), 3.69 (dd, 2H, J = 5.86, 6.10, 10.99, and 11.23 Hz), 3.96 (dd, 2H, J = 3.17, 3.42, 10.98, and 11.23 Hz), 4.92 (s, 4H), 6.78 (s, 4H), 7.45 (dd, 4H, J = 3.17, 3.18, 6.53, and 6.84 Hz), 8.27 (dd, 4H, J = 3.17, 3.42, 6.83, and 7.08 Hz) ppm.

Anal. calcd for $C_{38}H_{38}O_4$: C, 81.2%; H, 6.9%; O, 11.7%. Found: C, 81.7%; H, 6.9%; O, 11.5%

Synthesis of 1,4-Bis(3,5-dimethyl-4hydroxybenzyl)benzene

76.3 g of 2,6-dimethylphenol and 43.1 g of 1,4bishydroxymethylbenzene were dissolved in 350 mL of ethyl alcohol, then 200 mL of conc. hydrochloric acid was added. The solution was stirred at 50°C for 72 h. The solution was cooled at 10°C overnight. The solid precipitate was collected by filtration and recrystallized from toluene to obtain Bis-BZ in 33.5% yield $(174-179^{\circ}C \text{ mp})$.

IR (KBr): 3420, 2916, 1488, 1304, 1202, 1146, 1024, 834, 752 cm $^{-1}$. $^1H\text{-}NMR$ (acetone-d_6): δ 2.15 (s, 12H), 3.74 (s, 4H), 6.77 (s, 4H), 7.01 (s, 2H), 7.08 (s, 4H) ppm.

Synthesis of 1,4-Bis[3,5-dimethyl-4-(2,3-epoxypropyloxy)benzyl]benzene

34.5 g of Bis-BZ was dissolved in 400 mL of epichlorohydrin. The solution was heated at 70°C to obtain a homogeneous soluiton; and then to this solution, 8.3 g of 48% aqueous sodium hydroxide was added dropwise with stirring under reduced pressure (~ 20 kPa) for 4 h. During the reaction, produced water was removed from the solution by azeotropic distillation. The distilled epichlorohydrin was returned to the solution after separation with water. The solution was washed with water three times. The unreacted epichlorohydrin was removed from the organic phase by distillation under reduced pressure (~ 1.5 kPa). The Bis-EBZ was obtained in 96.8% yield. The epoxy equivalent weight was 232 g eq (229 g eq calcd; 83–89°C mp).

IR (KBr): 2920, 1486, 1216, 1146, 1022, 914, 860, 758 cm⁻¹. ¹H-NMR (acetone-d₆): δ 2.19 (s, 12H), 2.62 (dd, 2H, J = 2.44, 2.68, 5.12, and 5.37 Hz), 2.78 (dd, 2H, J = 4.15 and 5.12 Hz), 3.27 (m, 2H), 3.59 (dd, 2H, J = 6.34, 6.59, 10.98, and 11.22 Hz), 3.78 (s, 4H), 4.03 (dd, 2H, J = 2.68 and 11.22 Hz), 6.86 (s, 4H), 7.11 (s, 4H) ppm.

Anal. Calcd for $C_{30}H_{34}O_4$: C, 78.5%; H, 7.5%; O, 14.1%. Found: C, 78.6%; H, 7.5%; O, 14.0%

Preparation of Cured Polymers

Typical Procedure

Epoxy resin and phenol novolac were mixed at 150° C with a 1 : 1 equivalent ratio. To the obtained homogeneous mixture 1.2 wt % of triphenylphosphine was added, and the mixture was heated at 100°C by using a mixing roll apparatus. The mixture was cured at 150°C for 3 min, followed by postcuring at 180°C for 12 h.

Characterization and Measurements

Melting points were determined by a Büchi 535 melting point apparatus. Elemental analyses were carried out on a Heraeus CHN-O Rapid Analyzer. IR spectrum was examined using a Hitachi 270-50 IR spectrometer. ¹H-NMR spectrum was obtained from a JEOL GX-400 (400 MHz), where the sample was dissolved in chloroform-d₁, acetone- d_6 , or N,N-dimethylformamide- d_7 with tetramethylsilane employed as an internal standard. TMA measurement was carried out by a Seiko TMA SS10 at a heating rate of 10°C min under a nitrogen atmosphere. The CTE was obtained from the thermal expansion quantity. DMA measurement was performed in forced vibration at 11 Hz on an Orientec Rheovibron RHEO-2000 dynamic viscoelastic spectrometer at a heating rate of 10°C min under a nitrogen atmosphere. TGA measurement was made on a Seiko SSC 5200 TG/DTA 220 in a nitrogen atmosphere at a heating rate of 10°C min. Moisture absorption was performed by using a Tabai Espec TPC-410 pressure cooker tester. The quantity of absorbed water was determined by the weight difference before and after moisture absorption.

CONCLUSION

A new anthracene containing epoxy resin (Bis-EAT) was synthesized and was confirmed by the epoxy equivalent weight, EA, IR, and ¹H-NMR analyses. A cured polymer obtained from the new synthesized epoxy resin and phenol novolac showed higher T_g , higher moisture resistance, and lower thermal expansion. The pronounced good properties of the cured polymer from Bis-EAT should be originated from the condensed polynuclear aromatic structure of 9,10-anthrylene unit.

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