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

MASASHI KAJI,[1] KAZUHIKO NAKAHARA,[1] TAKESHI ENDO[2]

[1] Electronic Materials Research & Development Center, Advanced Materials Division, Nippon Steel Chemical Co., Ltd., 46-80, Nakabaru, Sakinohama, Tobata-ku, Kitakyusyu, 804-8503 Japan

[2] Research Laboratory of Resources Utilization, Tokyo Institute of Technology, 4259, Nagatsuta-cho, Midori-ku, Yokohama, 226-8503 Japan

ABSTRACT: A new type of epoxy resin containing a 4,4′-biphenylene moiety in the backbone (Bis-EBP) is synthesized and confirmed by elemental analysis, infrared spectroscopy, and ^{1}H-nuclear magnetic resonance spectroscopy. In addition, to evaluate the influence of the 4,4′-biphenylene group in the structure, an epoxy resin having a 1,4-phenylene group in place of the 4,4′-biphenylene moiety (Bis-EP) is synthesized. The cured polymer obtained through the curing reaction between the new biphenyl-containing epoxy resin and phenol novolac is used for making a comparison of its thermal and physical properties with those obtained from Bis-EP and bisphenol-A (4,4′-isopropylidenediphenyl)-type epoxy resin (Bis-EA). The cured polymer obtained from Bis-EBP shows markedly higher fracture toughness of 1.32 MPa m$^{1/2}$, higher glass transition temperature, lower moisture absorption, and higher thermal decomposition temperature. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 74: 690–698, 1999

Key words: epoxy resin; biphenyl derivative; thermal properties; fracture toughness

INTRODUCTION

Epoxy resins have been used in many industrial applications, such as surface coatings, adhesives, structural composites, printed circuit boards, and insulating materials for electronic devices, etc.,[1–2] because of their good heat and chemical resistance, and superior mechanical and electrical properties, in addition to their excellent processibilities. However, cured polymers from epoxy resins are relatively brittle with poor crack resistance. Therefore, there have been many studies on improving fracture toughness of epoxy polymers. The most widely known method is to incorporate a rubber material into an epoxy polymer matrix.[3–4] The rubber material precipitates out as a dispersed phase during the curing reaction. By this means, the fracture energy of the epoxy can be increased through rubber cavitation for plastic deformation and shear yielding in the matrix. Although the fracture toughness can be increased by applying this method, both mechanical strength and tensile modulus are reduced owing to the addition of soft inclusions into the matrix. Furthermore, some part of the rubber material can be miscible with the epoxy, which leads to decreased glass transition temperature (T_g) of the matrix.

To overcome these problems, incorporation of ductile engineering plastics with high T_g, such as polysulfones, poly(phenylene oxides), poly ether-imides and so on, has been studied in recent

years.[5–6] However, the engineering plastics in general have higher melting viscosity, which deteriorate the processibilities of the epoxy resins.

Therefore, an epoxy resin that gives a cured polymer with higher fracture toughness and T_g is required. Modifications of the backbone of epoxy resins has recently attracted much attention in attempts to enhance thermal properties.[7–8] Nevertheless, few studies have been reported on structural modification of epoxy resin for increased fracture toughness. In general, fracture toughness can be increased through decreasing crosslinking density, but T_g decreases. This means a trade-off exists between T_g and fracture toughness for the conventional epoxy resin system. We have reported that the incorporation of a symmetric rigid segment, such as 4,4'-biphenylene moiety or 2,6-naphthylene moiety, into the resin backbone, was effective for increasing fracture toughness and T_g.[9–10]

In this article, a new epoxy resin containing a 4,4'-biphenylene moiety was synthesized, and the properties of the cured polymer obtained from the new epoxy resin and phenol novolac were compared with those from an epoxy resin having a 1,4-phenylene group in place of the 4,4'-biphenylene moiety and a conventional bisphenol-A (4,4'-isopropylidenediphenol)-type epoxy resin.

EXPERIMENTAL

Materials

Commercially available phenol, 4,4'-diacetylbiphenyl, methyl lithium, toluene, and methyl isobutyl ketone (MIBK) were used without further purification. Ethyl ether and epichlorohydrin were distilled before use. 1,4-Bis(1-hydroxy-1-methylethyl)benzene (*p*-diol), bisphenol-A-type epoxy resin (Epikote 828), and phenol novolac (Tamanol 758) were obtained from Mitui Chemical Co. (Tokyo, Japan), Yuka Shell Epoxy Co. (Tokyo, Japan), and Arakawa Chemical Co. (Osaka, Japan), respectively. Triphenylphosphine as a curing accelerator was used as received from Hokko Chemical Co. (Tokyo, Japan).

Synthesis of 4,4'-Bis-(1-hydroxy-1-methylethylidene)biphenyl (BHBP)

Into 600 mL of ethyl ether was dissolved 37.7 g of 4,4'-diacetylbiphenyl. After the solution was cooled to 25°C, 300 mL of 1.1*M* methyl lithium

ethyl ether solution was added dropwise to this solution with stirring below 25°C. The reaction was continued at 25°C for 40 h. The solution was poured into 300 mL of water and stirred for 1 h. From the organic solution, the solid product was obtained by evaporation of ethyl ether and recrystallized from ethyl acetate to give BHBP in 96.0% yield. mp 166–168°C.
IR (KBr): 3364, 3092, 2980, 1498, 1394, 1378, 1362, 1262, 1164, 1138, 1098, 1006, 956, 866, 822, 734, 564 cm^{-1}. ^{1}H-NMR (acetone-d_6): δ 1.55 (s, 12H), 4.03 (s, 2H), 7.59 (s, 8H) ppm.

Synthesis of 4,4'-Bis-[1-(4-hydroxyphenyl)-1-methylethylidene]-biphenyl (Bis-BP)

BHBP (40.5 g) and phenol (211.5 g) were added to 200 mL of toluene in a 1000-mL three-necked flask and the solution was heated at 30°C. To this solution, 150 mL of concentrated hydrochloric acid was added with stirring. The reaction was continued at 30°C for 48 h. The solution was neutralized with aqueous sodium hydroxide. The aqueous phase was separated from organic phase and discarded. From the organic phase, toluene and unreacted phenol were removed by distillation under reduced pressure. During the distillation, the temperature was raised to 160°C. The residual product was recrystallized from toluene to give a white solid product. The obtained Bis-BP was dried at 50°C for 15 h *in vacuo* 58.0% yield. mp 195–198°C.
IR (KBr): 3636, 3264, 2972, 1616, 1514, 1364, 1252, 1180, 1086, 1006, 826, 566 cm^{-1}. ^{1}H-NMR (chloroform-d_1): δ 1.68 (s, 12H), 4.88 (s, 2H), 6.74 (*d*, 4H, *J* = 8.76 Hz), 7.13 (*d*, 4H, *J* = 8.76 Hz), 7.27 (*d*, 4H, *J* = 8.12 Hz), 7.47 (*d*, 4H, *J* = 8.33 Hz) ppm.

Synthesis of 4,4'-Bis{1-[4-(2,3-epoxypropyloxy)-phenyl]-1-methylethylidene}biphenyl (Bis-EBP)

Thirty grams of bis-BP was dissolved in 131.5 g of epichlorohydrin. The solution was heated at 70°C to obtain a homogeneous solution; then to this solution 11.6 g of 48% aqueous sodium hydroxide was added dropwise with stirring under reduced pressure (~ 20 kPa) for 4 h. During the reaction, generated water was removed from the solution as the epichlorohydrin azeotrope by distillation. The distilled epichlorohydrin was returned to the solution after separation with water. After the unreacted epichlorohydrin was distilled from the solution, MIBK was added to dissolve the product. Then to this solution 1.9 g of 20% aqueous

sodium hydroxide was added dropwise with stirring at 80°C. The reaction was continued for 2 h. The solution was washed with water three times, and the MIBK was distilled to give Bis-EBP in 96.5% yield. The epoxy equivalent weight (EEW) was 271 g/eq (calcd 267 g/eq).

IR (KBr): 2968, 1610, 1512, 1364, 1298, 1246, 1186, 1036, 918, 824, 572 cm^{-1}. ^{1}H-NMR(chloroform-d_1): δ 1.67 (s, 12H), 2.72 (dd, 2H, J = 2.68, 4.90 Hz), 2.87 (dd, 2H, J = 4.39, 4.63 Hz), 3.33 (quin, 2H, J = 3.17, 5.61 Hz), 3.93 (dd, 2H, J = 5.61, 10.98 Hz), 4.16 (dd, 2H, J = 3.17, 10.98 Hz), 6.82 (d, 4H, J = 6.83 Hz), 7.17 (d, 4H, J = 6.83 Hz), 7.25 (d, 4H, J = 6.34 Hz), 7.45 (d, 4H, J = 8.29 Hz) ppm.

ANAL. calcd for $C_{36}H_{38}O_4$: C, 80.9%; H, 7.2%; O, 12.0%. Found: C, 80.5%; H, 7.2%; O, 11.6%

Synthesis of 1,4-Bis[1-(4-hydroxyphenyl)-1-methylethylidene]-benzene (Bis-P)

The synthesis of Bis-P was treated in the same manner as the synthesis of Bis-BP, where BHBP was placed by *p*-diol. Bis-P was obtained in 89.4% yield. mp 192–194°C.

IR (KBr): 3608, 2972, 1616, 1516, 1250, 1184, 1018, 828, 586 cm^{-1}. ^{1}H-NMR(acetone-d_6): δ 1.61 (s, 12H), 6.72 (d, 4H, J = 8.78 Hz), 7.06 (d, 4H, J = 8.78 Hz), 7.12 (s, 4H), 8.10 (s, 2H) ppm.

Synthesis of 1,4-Bis{1-[4-(2,3-epoxypropyloxy)phenyl]-1-methyl-ethylidene}benzene (Bis-EP)

The synthesis of Bis-EP was treated exactly the same as the synthesis of Bis-EBP, where Bis-BP was placed by Bis-P. Bis-EP was obtained in 97.8% yield. The EEW was 233 g/eq (calcd 229 g/eq). mp 62–64°C.

IR (KBr): 2972, 1610, 1514, 1246, 1188, 1038, 916, 834, 580 cm^{-1}. ^{1}H-NMR (chloroform-d_1): δ 1.62 (s, 12H), 2.73 (dd, 2H, J = 2.68, 4.90 Hz), 2.88 (dd, 2H, J = 4.39, 4.63 Hz), 3.33 (quin, 2H, J = 3.17, 3.42 Hz), 3.95 (dd, 2H, J = 5.61, 10.98 Hz), 4.16 (dd, 2H, J = 3.42, 10.98 Hz), 6.81 (d, 4 H, J = 8.78 Hz), 7.08 (s, 4H), 7.14 (d, 4H, J = 8.78 Hz) ppm.

ANAL. calcd for $C_{30}H_{34}O_4$: C, 78.6%; H, 7.5%; O, 14.0%. Found: C, 78.2%; H, 7.5%; O, 13.7%

Preparation of Cured Polymers

Typical Procedure. Epoxy resin and phenol novolac were mixed at 150°C with a 1 : 1 equiv. To the obtained homogeneous mixture 1.2 wt % of triphenylphosphine was added and mixed by using a mixing roll apparatus at 100°C. The mixture

was cured at 150°C for 3 min, followed by post-curing at 180°C for 12 h.

Characterization and Measurements

The melting points were determined by a Büchi 535 melting point apparatus. Elemental analyses (EA) were carried out on a Heraeus CHN-O rapid analyzer. Infrared (IR) spectrum was examined using a Hitachi 270-50 infrared spectrometer. ^{1}H-nuclear magnetic resonance (^{1}H-NMR) spectrum was obtained from a Jeol JNM-LA400 (400 MHz), where a sample was dissolved in acetone-d_6 or chloroform-d_1 with tetramethylsilane employed as an internal standard. Thermomechanical analysis (TMA) was carried out by a Seiko TMA SS10 at a heating rate of 10°C/min under a nitrogen atmosphere. The coefficient of linear thermal expansion (CTE) was obtained from the thermal expansion quantity. Dynamic mechanical analysis (DMA) was performed in a 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. Crosslinking density (ρ) was determined according to the rubber elasticity theory as follows:[11]

$$\rho = E'/3\phi RT \qquad (1)$$

where E' is a storage modulus of a cured polymer at a peak temperature of tan δ + 50°C, ϕ is a front factor (assumed as ϕ = 1), R is the gas constant, and T is an absolute temperature. The density of a cured polymer was obtained by a sink-and-float method using a Mirage densimeter at 20°C. The reciprocal of the density was assumed to be the specific volume. Thermogravimetric analysis (TGA) was made on a Seiko 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 water absorbed was determined by the weight difference before and after moisture absorption. Fracture toughness was estimated by critical stress intensity factor (K_{IC}) according to the three-point bending method.[12] Flexural strength and modulus were measured on a Shimazu AG-500 according to JIS K-6911.

RESULTS AND DISCUSSION

Synthesis of Biphenyl-Containing Epoxy Resin

The new biphenyl-containing epoxy resin, 4,4′-bis{1-[4-(2,3-epoxypropyloxy)phenyl]-1-methyl-

Scheme 1 Synthesis of Bis-EBP.

Figure 2 ¹H-NMR spectrum of Bis-EBP.

ethylidene}biphenyl (Bis-EBP), was prepared through the following three steps. Syntheses of BHBP, Bis-BP, and epoxidation of Bis-BP according to **Scheme 1** were carried out.

BHBP was synthesized through the reaction of 4,4′-diacethlbiphenyl and methyl lithium, followed by hydrolysis with water. In the ¹H-NMR spectrum of BHBP, all signals corresponding to the proposed structure were observed in acetone-d_6. Namely, two singlet signals attributable to the methyl and the hydroxy protons were observed at 1.55 and 4.03 ppm, respectively. The singlet corresponding to the aromatic protons could be observed at 7.59 ppm, suggesting that all the protons on the biphenyl ring are equivalent. In the IR spectrum of BHBP, the typical absorption band of the hydroxy group was observed at 3364 cm^{-1}, and the characteristic absorption at

around 1700 cm^{-1} for the carbonyl group in 4,4′-diacetylbiphenyl has disappeared. The melting point of BHBP was 166–168°C. Valyi et al. had synthesized BHBP through the reaction of 4,4′-diacetylbiphenyl with methyl magnesium iodide in toluene.[13] The determination of the structure of BHBP was performed by the spectral analyses in addition to the melting point.[13]

Bis-BP was obtained as a white crystal by the condensation reaction of phenol with BHBP in toluene in a 58.0% yield. To enhance the selectivity at the *p* position of phenol, an excess amount of phenol was used to BHBP and a lower temperature of 30°C was applied. Isomers reacted at *o* position of phenol and oligomeric

Figure 1 IR spectrum of Bis-EBP.

Scheme 2   Synthesis of Bis-EP.

products were generated even in this condition, which reduced the yield of the desired product. In the ^{1}H-NMR spectrum of Bis-BP in chloroform-d_1, two singlet signals were observed at 1.68 and 4.88 ppm, which were attributable to the methyl protons and the hydroxy protons. Further, four kinds of doublet peaks corresponding to the aromatic protons were detected at 6.74, 7.13, 7.27, and 7.47 ppm, respectively. These results are consistent with the proposed structure shown in **Scheme 1.**

As shown in Figure 1 (IR spectrum of Bis-EBP), the characteristic band of the oxirane ring

was observed at 918 cm^{-1}. The ^{1}H-NMR spectrum in chloroform-d_1 is shown in Figure 2. The same signal pattern as in Bis-BP was observed except for the signals corresponding to the glycidyl group. Assignments of the chemical shifts are as follows: 1.67 ppm (singlet, methyl protons), 6.82 and 7.17 ppm (double doublet, phenoxy ring protons), 7.25 and 7.45 ppm (double doublet, biphenyl ring protons), and 2.72–4.16 ppm (glycidyl group protons). The EA results were in good agreement with the calculated values. The EEW of Bis-EBP was found to be 271 g/eq (calcd 267 g/eq). The structure of Bis-EBP was confirmed by the spectral analyses, the EA, and the EEW.

To examine the influence of the 4,4′-biphenylene moiety in the main chain, 1,4-bis{1-[4-(2,3-epoxypropyloxy)phenyl]-1-methylethylidene}-benzene (Bis-EP), which has a 1,4-phenylene group in place of the 4,4′-biphenylene moiety, was synthesized through the following two steps. Synthesis and epoxidation of Bis-P according to **Scheme 2** were carried out.

In the ^{1}H-NMR spectrum of Bis-P in acetone-d_6, three singlet signals were observed at 1.61, 7.12, and 8.10 ppm, which were attributable to the methyl protons, the aromatic protons on the phenylene ring, and the hydroxy protons, respectively. Two kinds of doublet peaks corresponding to the aromatic protons on the phenol ring were

Table I   Thermomechanical Analysis of Cured Polymers

Epoxy Resin	A[b]	$T_{g_{TMA}}$ (°C)	CTE[a] ($\times 10^{-5}$, °C^{-1}) Glassy Region	Rubbery Region
Bis-EBP		147	6.3	16.8
Bis-EP		131	6.4	17.4
Bis-EA		128	6.2	17.1

[a] Coefficient of linear thermal expansion.

[b] CH$_2$CHCH$_2$O—⟨ ⟩—A—⟨ ⟩—OCH$_2$CHCH$_2$.

Figure 3 DMA results of the cured polymers. (—○—) Bis-EBP polymer, (—□—) Bis-EP, (—△—) Bis-EA.

detected at 6.72 and 7.06 ppm. The melting point of Bis-P was 192–194°C. Broderick et al. prepared Bis-P by treating p-diol with excess phenol saturated with gaseous hydrochloric acid at 30–70°C.[14] The structure of Bis-P was determined by the spectral analyses in addition to the melting point.[12]

In the IR spectrum of Bis-EP, the characteristic band of the oxirane ring was observed at 916 cm^{-1}. In the ^{1}H-NMR spectrum of Bis-EP in chloroform-d_1, the same signal pattern as in Bis-P was observed except for the signals corresponding to the glycidyl group. Assignments of the chemical shifts are as follows: 1.63 ppm (singlet, methyl protons), 7.08 ppm (singlet, aromatic protons on phenylene ring), 6.81 and 7.14 ppm (doublet, aromatic protons on phenoxy ring), and 2.72–4.18 ppm (multiplet, glycidyl group protons). The EA results were in good agreement with the calculated values. The EEW of Bis-EP was found to be 233 g/eq (calcd 229 g/eq). These results might support the structure of Bis-EP shown in **Scheme 2.**

Properties of Cured Polymers

To examine the influence of the 4,4′-biphenylene moiety in the resin backbone on the thermal and physical properties, the cured polymers were pre-

pared from the new biphenyl-containing epoxy resin (Bis-EBP), phenyl-containing epoxy resin (Bis-EP), and bisphenol-A–type epoxy resin (Bis-EA) using phenol novolac (PN) as a curing agent [i.e., Bis-EBP/PN (Bis-EBP polymer), Bis-EP/PN (Bis-EP polymer), and Bis-EA/PN (Bis-EA polymer)].

The TMA results are summarized in Table I. The inflection point of the thermal expansion was defined as $T_{g_{TMA}}$. Bis-EBP polymer gave the highest $T_{g_{TMA}}$ followed by Bis-EP and Bis-EA polymer in this order. Figure 3 shows the DMA spectra, and the results are summarized in Table II. Although the maximum temperature of the loss modulus (G'') should be taken as T_g, the peak temperature of tan δ was assumed to be T_g and expressed as $T_{g_{DMA}}$ in this article. Crosslinking density of the cured polymers were calculated according to the rubber elasticity theory,[11] and the results are summarized in Table II. We have reported that the T_g rises as the crosslinking density increases in the conventional epoxy resin systems.[9] Although the Bis-EBP polymer has the lowest crosslinking density of the cured polymers, Bis-EBP polymer gave the highest $T_{g_{DMA}}$. In the Bis-EBP polymer, the stiffness of the 4,4′-biphenylene skeleton in the main chain may restrict the thermal movement of the polymer backbone.

Table II   Dynamic Mechanical Analysis of Cured Polymers

| Epoxy Resin | $T_{g_{DMA}}$ (°C) | Storage Modulus (GPa) | | $M_c{}^{c}$ | ρ^{d} (10^{-3} mol/ cm³) |
		Glassy Region[a]	Rubbery Region[b]		
Bis-EBP	172	2.27	0.024	620	1.93
Bis-EP	154	2.25	0.031	460	2.63
Bis-EA	142	2.30	0.032	420	2.89

[a] Storage modulus at 30°C.
[b] Storage modulus at $T_{g_{DMA}}$ + 50°C.
[c] Molecular weight between crosslinking points.
[d] Crosslinking density.

Incorporation of the 4,4′-biphenylene group in the main chain may enhance the T_g of the cured polymer obtained from Bis-EBP.

The physical properties of the cured polymer are depicted in Table III. Bis-EBP polymer showed markedly higher fracture toughness of 1.32 MPa · m$^{1/2}$. We have reported that the cured polymer obtained from diglycidyl ether of 4,4′-dihydroxybiphenyl (4,4′-DHB) polymer which has the 4,4′-biphenylene group in the main chain exhibited higher fracture toughness.[9] It has been considered that the 4,4′-DHB polymer has a large free-volume fraction caused by the packing prevention of the main chain arising from a cooperative effect of the rigid 4,4′-biphenylene structure and the crosslinking points. The higher fracture toughness of the 4,4′-DHB polymer has been considered to depend on a plastic deformation enlarged by the large free-volume fraction.[9] As shown in Table IV, bis-EBP polymer has a larger specific volume than other polymers. These results might support the theory that Bis-EBP polymer has a larger free-volume fraction. The excellent fracture toughness of Bis-EBP polymer is presumably due to a large free-volume fraction caused by the packing prevention of the main chain in terms of the rigid 4,4′-biphenylene structure, in addition to the lower crosslinking density arising from incorporation of the biphenyl group

having large molecular weight. The lower flexural modulus was observed in Bis-EBP polymer, which seems to correspond to the larger free-volume fraction of Bis-EBP polymer.

The thermal stability of the cured polymers is compared by the temperature of 10% weight loss ($T_{10\%}$) and percentage of char yield at 700°C in TGA measurements. The TGA curves are shown in Figure 4, and the results are summarized in Table V. Although the anaerobic char yields of the polymers gave almost the same values around 19%, Bis-EBP polymer showed the highest $T_{10\%}$, which might be attributed to the restricted molecular mobility in the main chain arising from the stiffness of the 4,4′-biphenylene skeleton. Bis-EP polymer showed lower $T_{10\%}$ than Bis-EA polymer, which was presumably due to the looser crosslinking network in Bis-EP polymer.

The moisture absorption of the cured polymers is shown in Table III. Bis-EBP polymer gave the lowest moisture absorption of the cured polymers. There are many discussions about moisture absorptivity of cured polymers. Danieley et al.[15] reported that the saturated moisture absorption depends on the concentration of polar groups in the cured polymers. By contrast, Wang and Broutman[16] noted that the initial moisture absorption rate mainly depends on the free-volume fraction. Moreover, Diamont et al.[17] pointed out that the

Table III   Properties of Cured Polymers

Epoxy Resin	Flexural Strength (MPa)	Flexural Modulus (GPa)	Fracture Toughness (MPa m$^{1/2}$)	Moisture Absorption[a] (wt %)
Bis-EBP	113	2.84	1.32	1.39
Bis-EP	118	2.89	0.98	1.52
Bis-EA	118	3.09	0.76	1.96

[a] 133°C, 3 atm, 96 h.

Table IV Specific Volume of Cured Polymers

Epoxy Resin	Specific Volume (cm^3/g)
Bis-EBP	0.835
Bis-EP	0.828
Bis-EA	0.825

Table V Thermogravimetric Analysis of Cured Polymers

Epoxy Resin	Temperature of 10 wt % Weight Loss (°C)	Char Yield at 700°C (%)
Bis-EBP	412	19.0
Bis-EP	394	18.7
Bis-EA	403	18.5

network structure, the polymer polarity, the polymer morphology, and the microdamages of the polymers should be considered. The above result seems to depend on the hydrophobic nature of the biphenyl group, and the lower functionality of Bis-EBP. However, it is not clear which of the above factors or a combination thereof dominates the moisture absorptivity of the cured polymers in this stage.

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.[18] This information may mean that it is difficult to decrease the moisture absorption with keeping higher T_g in the conventional resin systems. However, incorporation of a rigid 4,4′-biphenylene structure into epoxy-cured polymer was effective for improving moisture re-

sistance and thermal stability in addition to fracture resistance.

CONCLUSIONS

A new biphenyl-containing epoxy resin (Bis-EBP) was synthesized and confirmed by EEW, EA, IR, and ^{1}H-NMR analyses. A cured polymer obtained from the new synthesized epoxy resin and phenol novolac showed higher fracture toughness, higher T_g, lower moisture absorption, and higher thermal decomposition temperature. The pronounced good properties of the cured polymer from Bis-EBP should be associated with the rigid 4,4′-biphenylene unit.

Figure 4 TGA thermograms of the cured polymers from Bis-EBP, Bis-EP, and Bis-EA.

REFERENCES

1. Lee, H.; Neville, K. Eds., Handbook of Epoxy Resins; McGraw-Hill: New York, 1972.
2. Sultan, J. N. Handbook of Composites; Van Nostrand–Reinhold: New York, 1982.
3. Sultan, J. N.; Laible, R. C.; MacGarry, F. J. J Appl Polym Sci 1971, 6, 127.
4. Bascom, W. D.; Cottington, R. L.; Jones, R. L.; Peyser, P. J Appl Polym Sci 1975, 19, 2545.
5. Bucknall, C. B.; Gillbert, A. H. Polymer 1989, 30, 213.
6. Pearson, R. A.; Yee, A. F. Polym Mater Sci Eng 1990, 63, 311.
7. Ichino, T.; Hasuda, Y. J Appl Polym Sci 1987, 34, 1667.
8. Shau, M. D.; Wang, T. S. J Polym Sci Part A: Polym Chem 1996, 34, 387.
9. Kaji, M. ACS Symposium Series 579, American Chemical Society, Washington, DC, 1994; p 220.
10. Kaji, M.; Yamada, Y. IUPAC International Symposium, Preprints, 1989, p 123.
11. Kinjo, N.; Ogata, M.; Numata, S.; Yokoyama, T. J Thermoset Plast Jpn 1985, 6(3), 31.
12. Yee, A. F.; Pearson, R. A. J Mater Sci 1986, 21, 2462.
13. Valyi, I.; Janssen, A. G.; Mark, H. J Phys Chem 1945, 49, 461.
14. Broderick, G. F.; Oxenrider, B. C.; Vitrone, J. (to Allied Chemical Corp.) U.S. Pat. 3,393,244, 1961.
15. Danieley, N. D.; Long, E. R. J Polym Sci, Polym Chem Ed 1981, 19, 2443.
16. Wang, T. C.; Broutman, L. J. Polym Eng Sci 1985, 25, 529.
17. Diamont, Y.; Marom, G.; Broutman, L. J. J Appl Polym Sci 1986, 26, 3015.
18. Ogata, M.; Kinjo, N.; Kawata, T. J Appl Polym Sci 1993, 48, 583.