Curing Kinetics and Thermal Properties of Diglycidylether of Bisphenol A with Various Diamines

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ABSTRACT: To prepare a high-performance epoxy, we synthesized three types of diamines {N,N'-(4,4'-diphenylether)-bis(4-aminophthalimide), 4,4'-bis(p-aminophenoxy)dibenzalphentaerythriol, and 2,2'-bis[4-(p-aminobenzoyl)phenyl]propane} as epoxy curing agents with a two-step reaction sequence. The structures of the synthesized diamines were confirmed with Fourier transform infrared and nuclear magnetic resonance spectroscopy. The curing kinetics and thermal stability of the cured epoxy resin with diglycidylether of bisphenol A were estimated with differential scanning calorimetry and thermogravimetric analysis under a nitrogen atmosphere. The kinetics parameters were determined with the Ozawa and Kissinger equations. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 81: 279–284, 2001

Key words: epoxy; diamine; curing kinetics; thermal stability; curing agent

INTRODUCTION

Epoxy resins have been commercially available for about 45 years and are now used in many major industrial applications, especially where technical advantages warrant their somewhat higher cost with respect to other thermosets. The characteristics of toughness, low shrinkage on curing, high adhesion to many substrates, good alkali resistance, and versatility in formulation make epoxy resins widely used in adhesive, laminating, coating, and casting applications. The chemistry and technological applications of epoxy resins are voluminous, and there are many new developments each year. To meet some application requirements, several approaches have been used to enhance the thermal properties of epoxy resins.[1,2]

The full characterization of the cure process of an epoxy resin involves many factors, that is, the properties and performance of the cured epoxy resin, which are dependent on the type of epoxy resin, the curing agent, and the curing conditions used. If the chemical structures of cured epoxy resins are constituted with aromatic rings, heterocyclic rings, or both, their thermal resistance is superior to those of constituents with flexible or aliphatic chains.[3]

To prepare high-performance epoxies, many researchers synthesized polymeric networks with a liquid-crystalline polymeric order. The resulting networks could be used in new applications because of their mechanical, electrical, and optical properties.[4–7] Liquid-crystalline epoxy networks were obtained mostly by chemical reactions between epoxy groups contained in the liquid-crystalline compounds and the curing agent. Another way to improve the thermal resistance of epoxy

resins is to use a curing agent containing imide, urethane,[8] or heterocyclic groups, such as hydroxyl-terminated imide compounds[9,10] and imide acid.[11,12]

In this article, we synthesized the various diamines as epoxy curing agents and investigated the curing behavior and resultant thermal resistance of cured epoxies with diglycidylether of bisphenol A (DGEBA).

EXPERIMENTAL

Materials

4-Aminophenyl ether (ODA) and 4-nitrobenzoyl chloride were purchased from the Fluka (Buchs, Switzerland). ODA was used after recrystallization in an ethanol/water mixture, and 4-nitrobenzoyl chloride was distilled under reduced pressure. 4,4′-Isopropyllidenediphenol (bisphenol A), 4-nitrophthalic anhydride, p-hydroxybenzaldehyde, 4-methoxyphenol, pentaerythritol, and Dowex 50W-X8 were purchased from Aldrich (Milwaukee, WI). Tetrahydrofuran (THF), toluene, benzene, dimethyl sulfoxide (DMSO), ethyl acetate, triethylamine, and dimethylacetamide (DMAc) were obtained from Aldrich and Jensei Chemical (Tokyo, Japan). DGEBA (YD-128S) was purchased from Kukdo Chemical Co., Ltd. (Seoul, Korea), and was used without further purification. The epoxy monomer was a viscous resin with an epoxide equivalent weight of 205–225 g/equiv (data furnished by the manufacturer).

Synthesis of N,N′-(4,4′-Diphenylether)-bis(4-aminophthalimide) (PEBAI)

A solution of ODA (2.0 g, 10.0 mmol) in DMAc was poured into a three-necked, round flask equipped with a Dean–Stark trap; then, a solution of 4-nitrophthalic anhydride (3.89 g, 20 mmol) in DMAc gradually was added. The mixture was stirred at room temperature for 2 days. After toluene was added, the temperature of the mixture was elevated to 150°C for 1 day. Stoichiometric water produced during the course of the reaction was collected with the Dean–Stark trap. Through the precipitation of the reaction mixture in distilled water and further washing with distilled water, pure N,N′-(4,4′-diphenylether)-bis(4-nitrophthalimide) was obtained. This product (4.70 g, 8.4 mmol) was added to 200 mL of DMAc containing 0.2 g of Pd/C (10%) and was reduced under a pressure of $5 kg_f/cm^2$ with hydrogen gas at 60°C for 1 day. After the reaction mixture was filtered and recrystallized in DMAc, PEBAI was obtained. The yield was 85%, and the melting temperature was 362°C.

Synthesis of 4,4′-Bis(p-aminophenoxy)dibenzalphentaerythriol (PABP)

Dowex 50w-X8 (1.53 g; a cation-exchange resin), benzene (100 mL), and DMSO (40 mL) were added to a three-necked, round flask equipped with a Dean–Stark trap and were heated to 120°C for 1 day. Then, pentaerythritol (8 g, 58.8 mmol), p-hydroxybenzaldehyde (15.07 g, 123.4 mmol), and p-toluenesulfonic acid (0.5 g) were added. By hot filtration, Dowex 50W-X8 was removed, and the reaction mixture was precipitated in benzene; pure 4,4′-dihydroxydibenzalphentaerythtitol (4HBP) was obtained. 4HBP (5.6 g, 16.2 mmol) was placed in a three-necked, round flask equipped with a reflux condenser, and to this flask, THF and triethylamine (5.8 g, 41.4 mmol) were added. A solution of 4-nitrobenzoyl chloride (6.3 g, 34.1 mmol) in THF was gradually added to a three-necked, round flask under a nitrogen atmosphere and then stirred at 80°C for 1 day. Through the evaporation of THF in the reaction mixture, the addition of distilled water, and further washing with distilled water, pure 4,4′-bis(p-nitrobenzoylether)dibenzalphentaerythritol (4PNBBP) was obtained. 4PNBBP (5.0 g, 9.5 mmol) was added to 30 mL of DMAc containing 0.12 g of Pd/C (10%) and was reduced under a pressure of $5 kg_f/cm^2$ with hydrogen gas at 70°C for 1 day. After the reaction mixture was filtered and recrystallized in an acetonitrile/ethyl acetate mixture, PABP was obtained. The yield was 89%, and the melting temperature was 282°C.

Synthesis of 2,2′-Bis[4-(p-aminobenzoyl)phenyl]propane (2BBPP)

Bisphenol A (10.0 g, 43.8 mmol) was placed in a three-necked, round flask equipped with a reflux condenser, and to this flask were added THF and triethylamine (15.5, 60.0 mmol). A solution of 4-nitrobenzoyl chloride (17.9 g, 50.0 mmol) in THF was gradually added to a three-necked, round flask under a nitrogen atmosphere and then stirred at 80°C for 1 day. Through the evaporation of THF in the reaction mixture, the addition of distilled water, and further washing with distilled water, pure 2,2′-bis[4-(p-nitribenzoyl)phenyl]propane (4NBPP) was obtained.
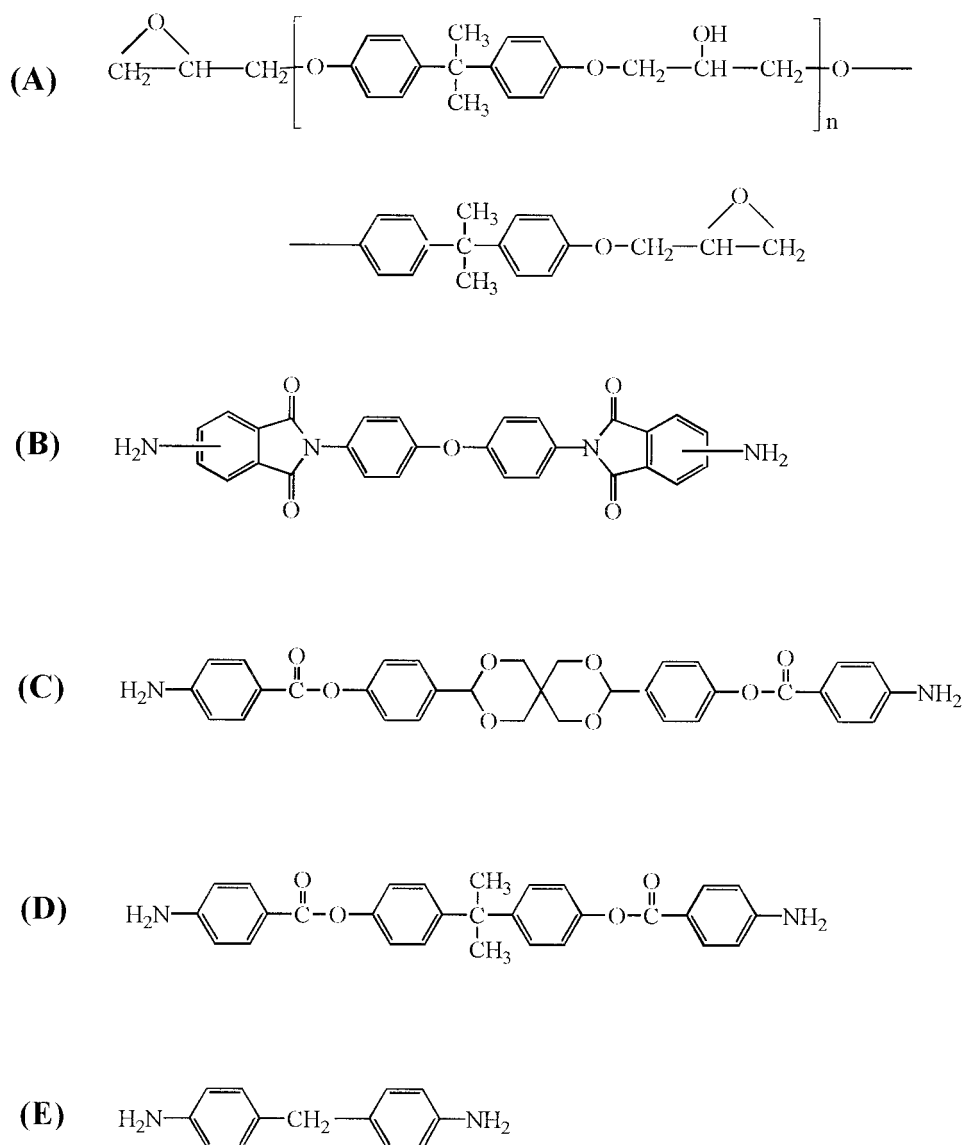
Figure 1 Structures of the various diamines and the epoxy resin used in this study: (A) DGEBA epoxy, (B) PEBAI, (C) PABP, (D) 2BBPP, and (E) DDM.

4NBPP (5.0 g, 9.5 mmol) was added to 100 mL of DMAc containing 0.12 g of Pd/C (10%) and was reduced under a pressure of $5kg_f/cm^2$ with hydrogen gas at 70°C for 1 day. After the reaction mixture was filtered and recrystallized in an acetonitrile/ethyl acetate mixture, 2BBPP was obtained. The yield was 77%, and the melting temperature was 272°C.

The structures of all diamines and the epoxy used in this article are shown in Figure 1.

Characterization and Sample Preparation

Nuclear magnetic resonance (NMR) spectra were obtained on a Bruker DPX 300-MHz ^{1}H-NMR spectrometer. Fourier transform infrared (FTIR) spectra were recorded on a Nicolet Magna-550 FTIR spectrometer (Madison, WI). The melting temperatures of the diamine products were measured with a Yanaco MP-S3 (Kyoto, Japan). Thermal analysis was carried out with differential scanning calorimetry (DSC; Mettler Toledo-7) (Greifensee, Switzerland) and thermogravimetric analysis (TGA; Shimazu TG-50) (Tokyo, Japan) under a nitrogen atmosphere. The calibrations of the instruments were performed with standard materials. DGEBA and the diamine curing agents were mixed at elevated temperatures and then stirred homoge-

neously. The amount of the curing agent was 50 mol % for DGEBA epoxy.

RESULTS AND DISCUSSION

Characterization of the Synthesized Diamines

The chemical structures of PEBAI, PABP, and 2BBPP were conformed by ^{1}H-NMR and FTIR:

PEBAI. ^{1}H-NMR (DMSO-d_6, ppm): 5.50–5.53 (s, amino groups, 4H), 5.79–5.85 (d, 2H), 5.95–5.97 (d, 2H), 6.10–6.16 (d, 4H), 6.36–6.41 (d, 4H), 6.51–6.56 (d, 2H). IR (KBr, cm^{-1}): 3360, 3456 (NH$_2$), 1712, 1763 (imide C=O), 3095 (aromatic C—H).

PABP. ^{1}H-NMR (DMSO-d_6, ppm): 3.30–3.35 (s, 8H), 4.56–4.63 (s, amino groups, 4H), 5.50–5.56 (s, 2H), 6.61–6.65 (d, 4H), 7.18–7.22 (d, 4H), 7.49–7.52 (d, 4H), 7.78–7.82 (d, 4H). IR (KBr, cm^{-1}): 3345, 3410 (NH$_2$), 2850, 2956 (aliphatic C—H), 1150, 1170, 1102, 1159, 1174, 1218 (spiroacetal C—O), 1710 (ester C=O), 1627 (aromatic C—C).

2BBPP. ^{1}H-NMR (DMSO-d_6, ppm): 0.63–0.65 (s, 6H), 5.07–5.13 (s, amino groups, 4H), 5.56–5.62 (d, 4H), 6.05–6.08 (d, 4H), 6.22–6.26 (d, 4H), 6.73–6.77 (d, 2H). IR (KBr, cm^{-1}): 3365, 3480 (NH$_2$), 1712 (ester C=O), 2870, 2961 (aliphatic C—H).

Through the structural characterization of FTIR, and NMR, we ascertained that the synthesized compounds were PEBAI, PABP, and 2BBPP.

Curing Kinetics and Thermal Properties

To obtain kinetic parameters such as the activation energy (E_a), we used the Ozawa equation [13] and the Kissinger equation.[14] The data from dynamic DSC measurements were analyzed with the following equation:

$$r = dx/dt = \beta dx/dt = A \exp(E/RT)(1 - x)^n \quad (1)$$

where E is the activation energy, R is the ideal gas constant, β is heating rate, A is preexponential factor and T is the temperature. Because the maximum rate takes place when dr/dt is 0, differentiating eq. (1) with respect to time and equating the resulting expression with zero give the following equation:
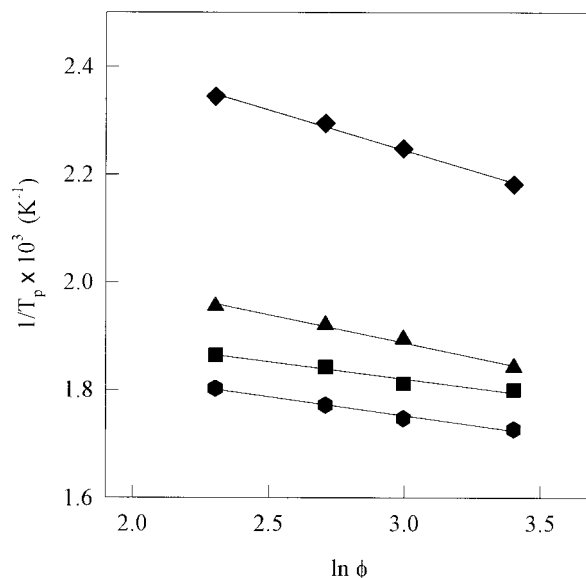

Figure 2   Plots for the determination of the E_a in the curing reaction via the Ozawa equation: (■) PEBAI, (●) PABP, (▲) 2BBPP, and (♦) DDM.

$$\beta E/RT_p^2 = An(1 - x)P^{n-1}\exp(E/RT_p) \quad (2)$$

where T_p is the maximum rate temperature. Equation (2) can be written in the natural logarithm form shown in eq. (3):

$$-\ln(\beta/T_p^2) = \ln(E/R) - \ln(An)$$
$$- (n - 1)\ln(1 - x)^p + E/RT_p \quad (3)$$

From the peak temperature and heating rate, we can obtain the data for a plot of $\ln(\beta/T_p^2)$ against $(1/T_p)$, a linear plot of $-\ln(\beta/T_p^2)$ versus $(1/T_p)$, as shown in Figure 2.

Another theoretical treatment, namely, Ozawa's method, can also be applied to the thermal data. He reported the following:

$$\text{Log } \beta = (1/2.303)\ln \beta = -0.4567(E/RT)$$
$$+ [\log(AE/R) - \log F(x) - 2.315] \quad (4)$$

where β is the heating rate and $F(x)$ is the conversion-dependent term. Thus, at the same conversion, a plot of $\ln \beta$ versus $1/T_p$ (Fig. 3) should be a straight line with a slope of $(2.303 \times 0.4567)E/R$.

Curing kinetics parameters obtained with a nonisothermal multiple scanning method are summarized in Table I. The scan rates (10, 15, 20, and 30°C/min) were used for the DGEBA/diamine
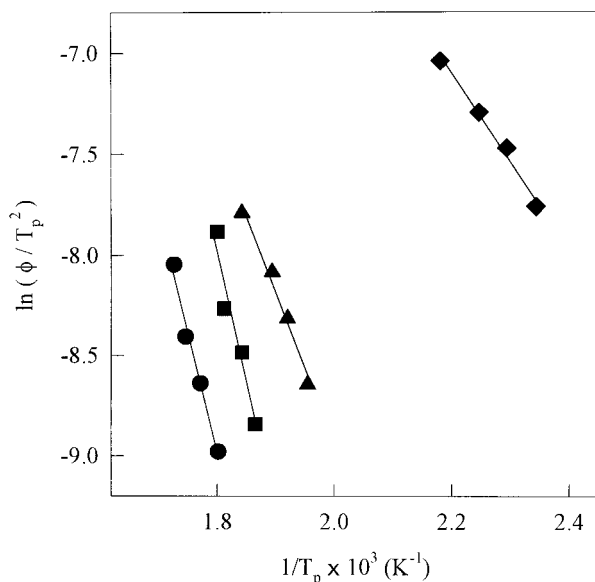
Figure 3 Plots for the determination of E_a in the curing reaction via the Kissinger equation: (■) PEBAI, (●) PABP, (▲) 2BBPP, and (♦) DDM.
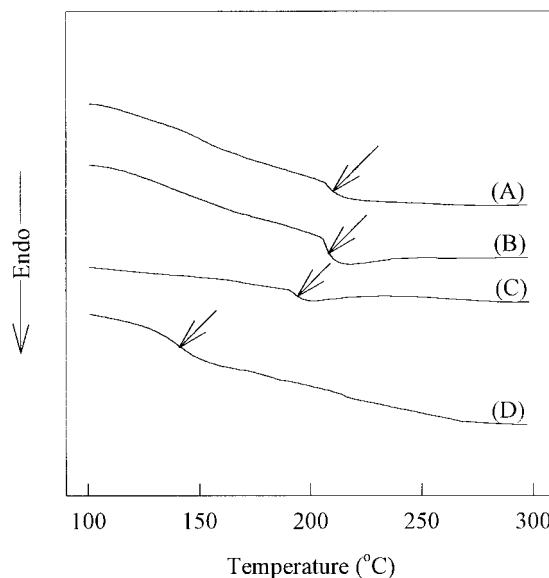

Figure 4 DSC thermogram of the cured DGEBA epoxy with various diamines: (A) PEBAI, (B) PABP, (C) 2BBPP, and (D) DDM

epoxies. In the DGEBA/4,4′-diaminodiphenylmethane (DDM) epoxy, E_a is similar to another result found for DGEBA/DDM (60.2 kJ/mol),[15] and the value is 55.6 kJ/mol by the Ozawa equation. However, E_a of the other epoxies—DGEBA/PEBAI, DGEBA/PABP, and DGEBA/2BBPP—is larger than for DGEBA/DDM. Therefore, it is reasonable to propose that the chemical reactivity of these four curing agents toward the DGEBA-type epoxy resin is DDM > 2BBPP > PEBAI > PABP. The curing peak temperatures for PEBAI, PABP, 2BBPP, and DDM with DGEBA epoxy are shown in Table I. The decreasing order at the higher curing peak temperature was PEBAI > PABP > 2BBPP > DDM. The synthesized diamines exhibiting a higher curing peak temperature under the same set of curing conditions have lower reactivity toward DGEBA-type epoxy resins. This result was similar to the E_a result.

We investigated the glass-transition temperatures (T_g's) of cured DGEBA/diamine epoxies with DSC measurements, and they are shown in Figure 4 and Table I. The DSC thermograms were recorded at a heating rate of 40°C/min, and the T_g was taken as the inflection point of the specific heat increment. The T_g's of the cured epoxies with synthesized diamines, except for DDM, were greater than 190°C. These results imply that the elasticity of the epoxy was improved through the incorporation of synthesized diamine elements.

Thermal Stability

Figure 5 shows the thermogravimetric (TG) thermogram of the cured epoxy with various diamines under a nitrogen atmosphere. The cured epoxy sustained thermal resistance up to 340°C without a significant weight loss.

Van Krevelen[16] proposed that the char residue from pyrolysis is linearly proportional to the oxygen index of halogen-free polymers. Increasing char formation can limit the production of combustible gases, decrease the exothermicity of the pyrolysis reaction, decrease the thermal conductivity of the burning materials, and, consequently, limit the flammability of the materials.
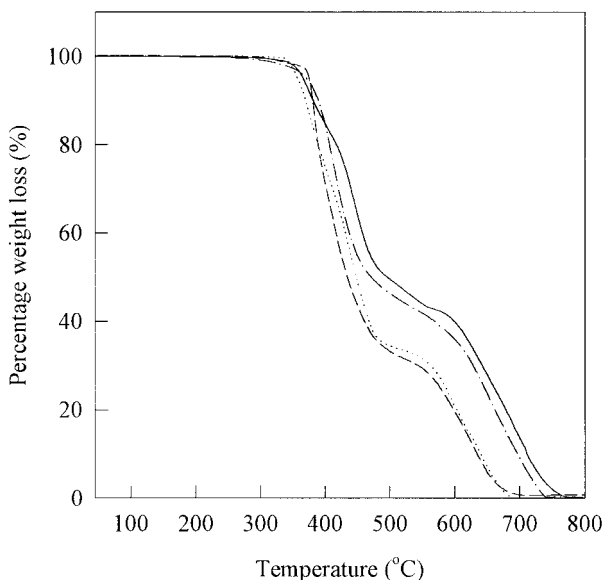
Table I Thermal Characteristics and Kinetic Parameters of Cured DGEBA Epoxy with Various Diamines

Diamine	T_g (°C)	T_p[a] (°C)	E_a (kJ/mol) By Ozawa Equation	By Kissinger Equation
PEBAI	209.0	299.6	118.8	99.2
PABP	207.7	279.2	133.9	109.4
2BBPP	193.1	254.6	82.0	62.9
DDM	140.3	172.4	55.6	36.4

[a] Curing peak temperature was measured under 20°C/min.

Figure 5 TG thermogram of the cured DGEBA epoxy with various diamines: (—) PEBAI, (— · —) PABP, (- - -) 2BBPP, and (– – –) DDM.

The char yields of cured DGEBA epoxy with PE-BAI, PABP, 2BBPP, and DDM at 500°C were 49.4, 46.2, 34.5, and 32.9 wt %, respectively. In comparison with the various diamines, the char yield of the DGEBA/PEBAI cured epoxy was the highest. This high char yield implies that incorporating imide into the epoxy matrix moiety elevates the flame retardancy of the epoxy.

CONCLUSIONS

To obtain a high-performance epoxy, we successfully synthesized three types of diamines, PEBAI, PABP, and 2BBPP, as epoxy curing agents with a two-step reaction sequence. Although the synthe-

sized diamines showed a low reactivity with DGEBA according to results from the kinetics equation, the epoxies cured with the diamines had higher T_g's and much greater char yields than the epoxy cured with DDM. For PEBAI, the introduction of am imide group into the network structure produced good flame retardancy.

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