Synthesis, Characterization, and Properties of Multifunctional Naphthalene-Containing Epoxy Resins Cured with Cyanate Ester

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ABSTRACT: Multifunctional naphthalene-containing epoxy resins derived from 2,7-dihydroxylnaphthalene were synthesized and the intermediates were characterized by Fourier transform infrared spectroscopy, elemental analysis, and mass spectrometry. The cured products from naphthalene-containing epoxy resin and the dicyanate ester of bisphenol A (DCBA) exhibited a better T_g and a lower coefficient of thermal expansion than those of the commercial epoxy system. The glass transition temperature, thermal stability, and moisture absorption were found to increase with the epoxy functionality when naphthalene-containing epoxy resins were cured with DCBA. Thermogravimetric analyses revealed that the DCBA-cured system had a better thermal stability than that of the 4,4′-diaminodiphenylsulfone (DDS)-cured system. The addition of a metallic catalyst into the epoxy resin/cyanate ester system not only facilitated the cyclotrimerization of the cyanate ester but also the polyetherification of the epoxy resin. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 73: 1611–1622, 1999

Key words: naphthalene; epoxy resin; multifunctionality; cyanate

INTRODUCTION

Recently, with the high-speed demands in logic and microprocessing devices, the input/output (I/O) numbers (pin numbers) must be increased. Therefore, the trend of IC packaging has shifted from conventional insertion mount devices, such as the dual inline package (DIP), to surface-mount devices, such as the quad flat package (QFP), small outline package (SOP), and the ball grid array (BGA). For mounting on a printed circuit board, both the semiconductor and circuit board have to be exposed to high temperatures of 215–260°C during reflow soldering. Many problems have been seen after the soldering process, such as package cracking (popcorn phenomenon), delamination, and poor performance in humidity testing. Therefore, it is necessary to develop a high glass transition temperature (T_g), low moisture-absorbing, and low thermal expansion resin system for high-reliability semiconductor devices.[1] Recently, we reported[2,3] that the incorporation of the naphthalene group into the backbone of epoxy resin resulted in a high glass transition temperature, dimensional stability, and moisture-resistant material suitable for high-performance electronic application. The properties of a final thermoset depend not only on the structure of the epoxy resin but also on the type of the curing agent. Most studies performed to date have been devoted to epoxy resins cured with amine-terminal curing agents,[4–11] and not many articles have been devoted to epoxy resin/cyanate ester thermosets.[12–14] Aryl cyanate esters can be processed much like epoxy resins for many applications. Similarities to epoxy resin include no volatile polymerization by-products, stable B-stage resins, low

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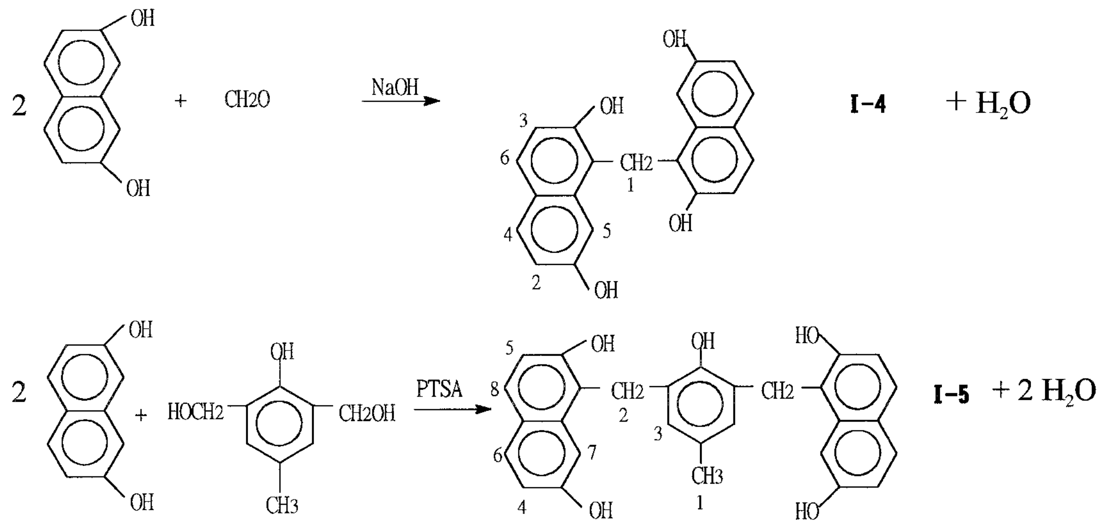


Figure 1 Schematic diagram of the synthesis of tetrafunctional (**I-4**) and pentafunctional (**I-5**) naphthalene-containing novolacs, and the assignments of carbon on ^{1}H-NMR for novolacs.

shrinkage, high adhesion, and void-free structures. High purity makes cyanate esters very attractive for use in electronic applications.[15] Kubens and Schulthier[16] found that cyanate ester resins were compatible and reactive with epoxy resins. The combinations of cyanate ester and epoxy resin can be formulated to yield cured products containing both triazine and oxazolidone ring structures.

The object of this study was to compare the thermal properties of cured products obtained from multifunctional naphthalene-containing epoxy resin, diglycidyl ether of bisphenol A, and *o*-cresol novolac formaldehyde epoxy resin cured with dicyanate of bisphenol A. The influence of the dicyanate ester and the metallic catalyst upon the epoxy thermoset is also discussed in this report.

EXPERIMENTAL

Materials

2,7-Dihydroxynaphthalene (Acros, Geel, Belgium), *p*-toluene sulfonic acid monohydrate (Ferak, Germany), epichlorohydrin (Janssen), bisphenol A (Acros), triethyl amine (TCI, Tokyo, Japan), copper acetylacetonate (TCI), *p*-nonylphenol (TCI), and 4,4′-diaminodiphenylsulfone (Janssen, Geel, Belgium) were all used as received. All solvents were obtained from various commercial sources and used without further purification unless otherwise noted.

Preparation of 1,1′-Bis(2,7-hydroxy-1-naphthyl)methane (I-4)

I-4 was synthesized according to the procedure reported.[2] A gray powdery product in 96% yield with a melting point of 253°C was obtained. The chemical structure of **I-4** was confirmed as follows: MS *m/e* 332 (65; M$^+$).

ANAL. Calcd for $C_{21}H_{16}O_4$: C, 75.88%; H, 4.85%. Found: C, 75.42%; H, 4.84%.

^{1}H-NMR (DMSO, d_6): δ 4.47 (s, 2H, C-1), δ 6.70–6.75 (dd, 2H, C-2), δ 6.95–6.99 (d, 2H, C-3), δ 7.37–7.47 (m, 6H, C-4, 5, 6). δ 9.15–9.68 (br, —OH).

Preparation of 2,6-Bis(2,7-dihydroxy-1-naphthylmethyl)-4-Methyl (I-5)

Into a 500-mL flask was added *p*-toluenesulfonic acid (PTSA, 0.34 g) and 200 mL MIBK. After purging with nitrogen for 10 min, 2,7-dihydroxynaphthalene (192.2 g, 1.2 mol) was added to the above solution at room temperature and mixed well. 2,6-Dimethylol-4-methyl phenol (mp = 124°C, produced in our lab, 33.64 g, 0.2 mol) was added portionwise over a period of 1 h. After completion of the addition, it was heated to 65°C and maintained at that temperature for 5 h. Aqueous sodium carbonate was added to the reaction mixture until the solution was neutral. The mixture was rotovapped at 195°C under reduced pressure to remove the unreacted 2,7-dihydroxynaphthalene and solvent. The crude solid

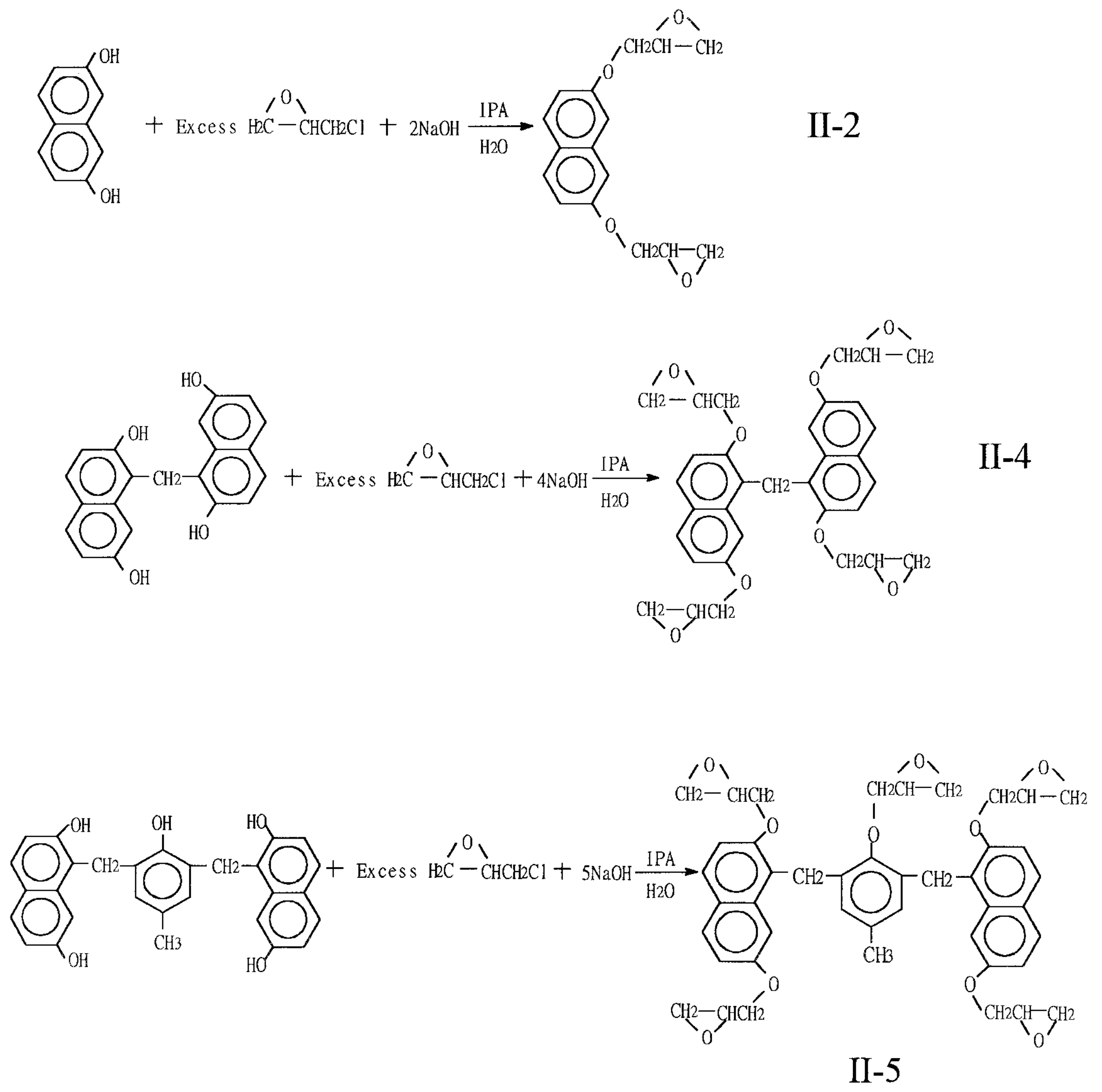


Figure 2 Schemes of the preparation of poly(glycidyl ether).

product was washed with a water/methanol (68/32, vol ratio) mixture many times to remove the residual 2,7-dihydroxynaphthalene. A gray product (75 g, 83% yield), mp 272–273°C, was obtained after vacuum-drying.

ANAL. Calcd for $C_{29}H_{24}O_5$: C, 76.98%; H, 5.35%. Found: C, 76.28%; H, 5.47%.

^{1}H-NMR (acetone, d_6): δ 1.88 (s, 3H, C-1), δ 4.27 (s, 4H, C-2), δ 6.60 (s, 2H, C-3), δ 6.88–6.94 (dd, 2H, C-4), δ 7.05–7.09 (d, 2H, C-5), δ 7.30–7.31 (d, 2H, C-6), δ 7.59–7.63 (d, 2H, C-7), δ 7.65–7.69 (d, 2H, C-8).

The assignments of carbon on the ^{1}H-NMR of corresponding novolacs are shown in Figure 1.

Preparation of Poly(glycidyl ether)s

Two commercial epoxy prepolymers, diglycidyl ether of bisphenol A [DGEBA, epoxy equivalent weight (EEW) 188] and *o*-cresol formaldehyde novolac epoxy (CNE, EEW 192) were generously supplied by the Nan-Ya Co. (Taipei, Taiwan) and Dow Chemical Co. (Freeport, TX), respectively. The procedures for the synthesis of multifunctional naphthalene-containing epoxy resins are described as follows and reaction schemes are shown in Figure 2.

Preparation of 2,7-Diglycidyloxynaphthalene (II-2)

Into a 500-mL four-neck round-bottom flask, equipped with a stirrer, heating mantle, thermo-

Table I Experimental Curing Formulations

Component	Epoxy Resins				
	DGEBA	CNE	**II-2**	**II-4**	**II-5**
EEW	188	192	148	168	161
Epoxy resin (g)	2.65	2.67	2.35	2.51	2.45
Cyanate ester (g)	2.35	2.33	2.65	2.49	2.55
Copper acetyl acetonate (g)	0.13	0.13	0.13	0.13	0.13
Nonylphenol (g)	0.13	0.13	0.13	0.13	0.13
Cyanate ester Weight percentage (wt %)	44.8	44.3	50.5	47.5	48.5

All experimental formulations were at the same equivalent ratio: cyanate group/epoxy group = 1.2/1.

couple, temperature controller, condenser, nitrogen inlet, and addition funnel, were charged 0.1 mol of 2,7-dihydroxynaphthalene, 1 mol of epichlorohydrin (ECH), 30 g of isopropyl alcohol (IPA), and 4 mL water. The reaction mixture was heated to 65°C while stirring and 20 wt % aqueous NaOH 40 g (0.2 mol) was added dropwise over a period of 45 min. After completion of the aqueous sodium hydroxide addition, the reaction mixture was maintained at 65°C for an additional 15 min and the bottom brine layer was removed by siphoning. The organic phase was further reacted with 20 wt % aqueous NaOH 20 g (0.1 mol) at 65°C for 30 min and then the phases were separated. The organic phase was washed several times with deionized water to remove the residual sodium chloride. The organic phase after water washes was placed on a rotary evaporator under a full vacuum at 150°C to remove the excess ECH and solvent completely. The EEW of the dark brown-colored semisolid product was determined and is listed in Table I.

Preparation of 1,1′-Bis(2,7-diglycidyloxy-1-naphthyl)methane (II-4) and 2,6-Bis(2,7-glycidyloxy-1-naphthyl-methyl)-4-methyl Glycidyl Phenyl Ether (II-5)

II-4 and **II-5** were synthesized by a procedure analogous to the synthesis of **II-2**. Both products were dark brown-colored solids. Corresponding EEWs were determined and the results are also shown in Table I.

Preparation of 2,2-Bis(4-cyanophenyl)propane or Dicyanate of Bisphenol A (DCBA)

To a three-neck 250-mL flask fitted with an overhead stirrer, thermometer, and dropping funnel was added 75 mL of acetone (dried over fresh 4 Å molecular sieves for 1 day). After cooling to −10°C, 11.64 g (110 mmol) of BrCN (caution: toxic!) was added and the solution was further cooled to −16°C. A solution of 11.95 g (52 mmol) of bisphenol A and 10.63 g (105 mmol) of triethylamine in 25 mL of acetone was prepared, transferred to a dropping funnel, and added dropwise with rapid stirring over a 40-min period while maintaining a reaction temperature of −16 ± 2°C. When the mixture had warmed to −5°C, it was rapidly filtered and the white ammonium bromide salt was washed with 25 mL of acetone. The combined filtrate and wash was diluted with 100 mL of cold CH_2Cl_2 and rapidly extracted with 100 mL of cold distilled water and twice with 100 mL of cold 1% NaCl. The CH_2Cl_2 phase was dried over anhydrous Na_2CO_3. The clear CH_2Cl_2 solution was then vacuum-distilled to yield a solid amber mass. This product was twice recrystallized from cold cyclohexane to yield 8.75 g (61%) of a white crystalline product: mp 81–82°C.

ANAL. Calcd for $C_{17}H_{14}O_2N_2$: C, 73.37%; H, 5.07%; N, 10.07%. Found: C, 73.34%; H, 5.03%; N, 9.91%.

^{1}H-NMR (DMSO-d_6): δ 1.61 (s, 6H, CH_3), δ 7.33–7.36 (d, 8H, phenyl). MS *m/e* 278 (28; M^+).

Measurement and Testing

^{1}H-NMR of the synthesized naphthalene-containing novolacs and DCBA were obtained on a Bruker Analytic WP-100. Samples were analyzed in deuterated acetone or deuterated DMSO using tetramethylsilane (TMS) as an internal standard. Elemental analyses were obtained from a Heraeus CHN-Rapid analyzer. Mass spectrometric analyses were performed on

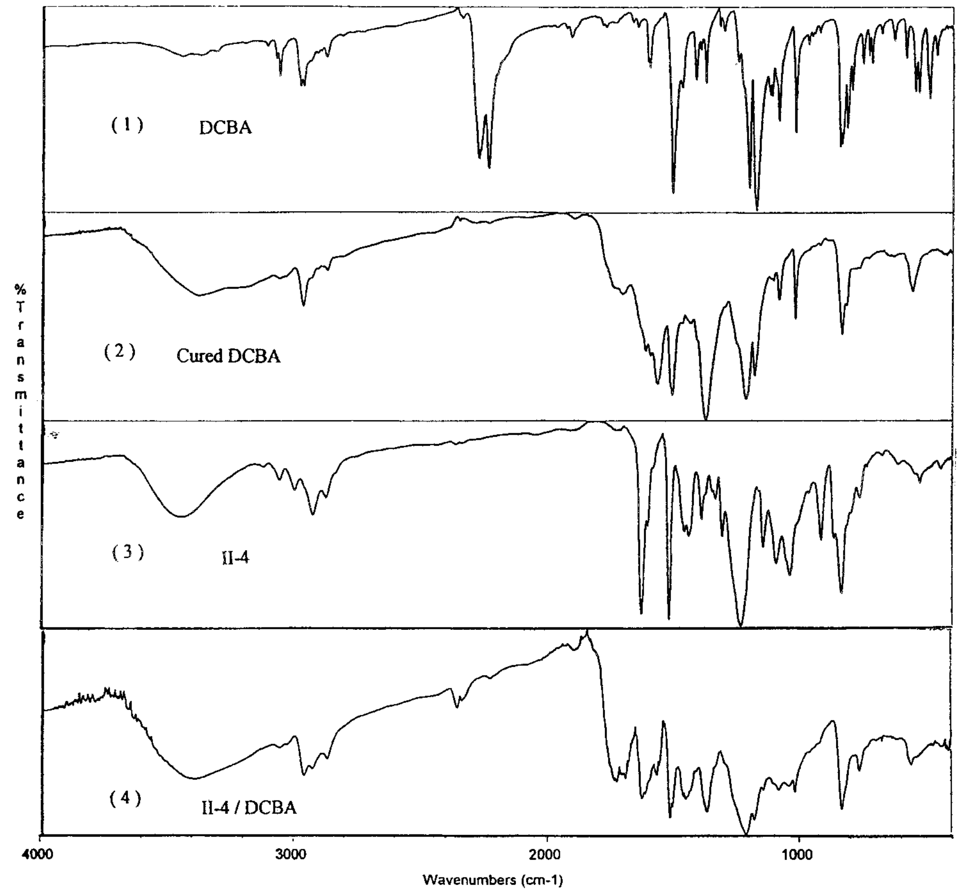


Figure 3 IR spectrum of (1) neat DCBA, (2) cured DCBA, using a copper acetylacetonate/nonylphenol mixture as a catalyst, (3) tetrafunctional naphthalene-containing epoxy resin **II-4**, and (4) tetrafunctional naphthalene-containing epoxy resin cured with DCBA, also using a copper acetylacetonate/nonylphenol mixture as a catalyst.

a VG 70-250S GC/MS spectrometer with a solid inlet. Infrared spectra were recorded with a Nicolet 520 FTIR spectrometer operated with a dry air purge. Signals of 32 scans at a resolution of 4 cm^{-1} were averaged before Fourier transformation. The EEWs of the epoxy resins were determined by the $HClO_4$/potentiometric titration method. Differential scanning calorimeter (Perkin–Elmer DSC-7) measurements were made at a scan rate of 10°C/min with 4–6-mg samples under a nitrogen atmosphere; the reaction exotherm can be traced from the change of the specific heat in the heat-flow curves, and ΔH is calculated. Dynamic viscoelastic properties were performed on a Perkin–Elmer 7 Series thermal analysis system with the DMA mode between 30 and 280°C, with a heating rate of 10°C/min at a frequency of 1 Hz. The temperature/time scan in a three-point bending mode was chosen. The dimension of the specimen was 20 × 12.7 × 1.5 mm, and the distance of the support span was 10 mm. The mechanical loss factor (tan δ) was determined. The coefficient of thermal expansion (CTE) was measured with the TMA module of the Perkin–Elmer 7 Series. A specimen 1.5 mm in thickness was used at the same heating rate of 5°C/min. The CTEs were calculated from the slope below the glass transition temperature. The thermal stability was obtained using a Perkin–Elmer thermogravimetric analyzer (TGA) with a heating rate of 20°C/min in a nitrogen atmosphere. The moisture pickup was determined by placing preweighed 2.5-mm-thickness × 45-mm-diameter cured disks in 23°C water for 10 days. The disks were removed and wiped off with a dry cloth and weighed to the nearest 0.001 g immediately. The density of the cured epoxy resin specimen was determined in a carbon tetrachloride–toluene density gradient column.

Curing Procedure of Epoxy Resins with DCBA

Commercial and synthesized epoxy resins were heated to 110°C under a full vacuum to drive off air bubbles and water in the epoxy resins.[17] Each epoxy resin was heated to 90–120°C to melt and then mixed well with the DCBA at the equivalent ratio of the cyanate group/epoxy group = 1.2/1, combined with copper acetylacetonate 2.5 parts and nonylphenol 2.5 parts (based on 100 parts of cyanate/epoxy mixtures); the formulations of thermosetting resins are listed in Table I. The mixtures were poured into an aluminum tray (20 × 14 × 5 mm) and cured in this mold under atmospheric pressure at 160°C/1 h and then post-cured at 200°C for 4 h to obtain specimens for property analyses.

RESULTS AND DISCUSSION

IR Analyses

The reaction of a difunctional cyanate ester and a difunctional glycidyl ether is quite complicated since many reactions are possible.[12] The complexity of the curing reaction increases with increasing functionality of the epoxy resins. The structure of the cured products will depend on the rate of each reaction and the initial equivalent ratio of the dicyanate ester and glycidyl ether.[13] In this study, the equivalent ratio of the cyanate group/epoxy group was fixed to a constant value (1.2/1) and the curing conditions were set in the same in order to simplify the scope of the discussion.

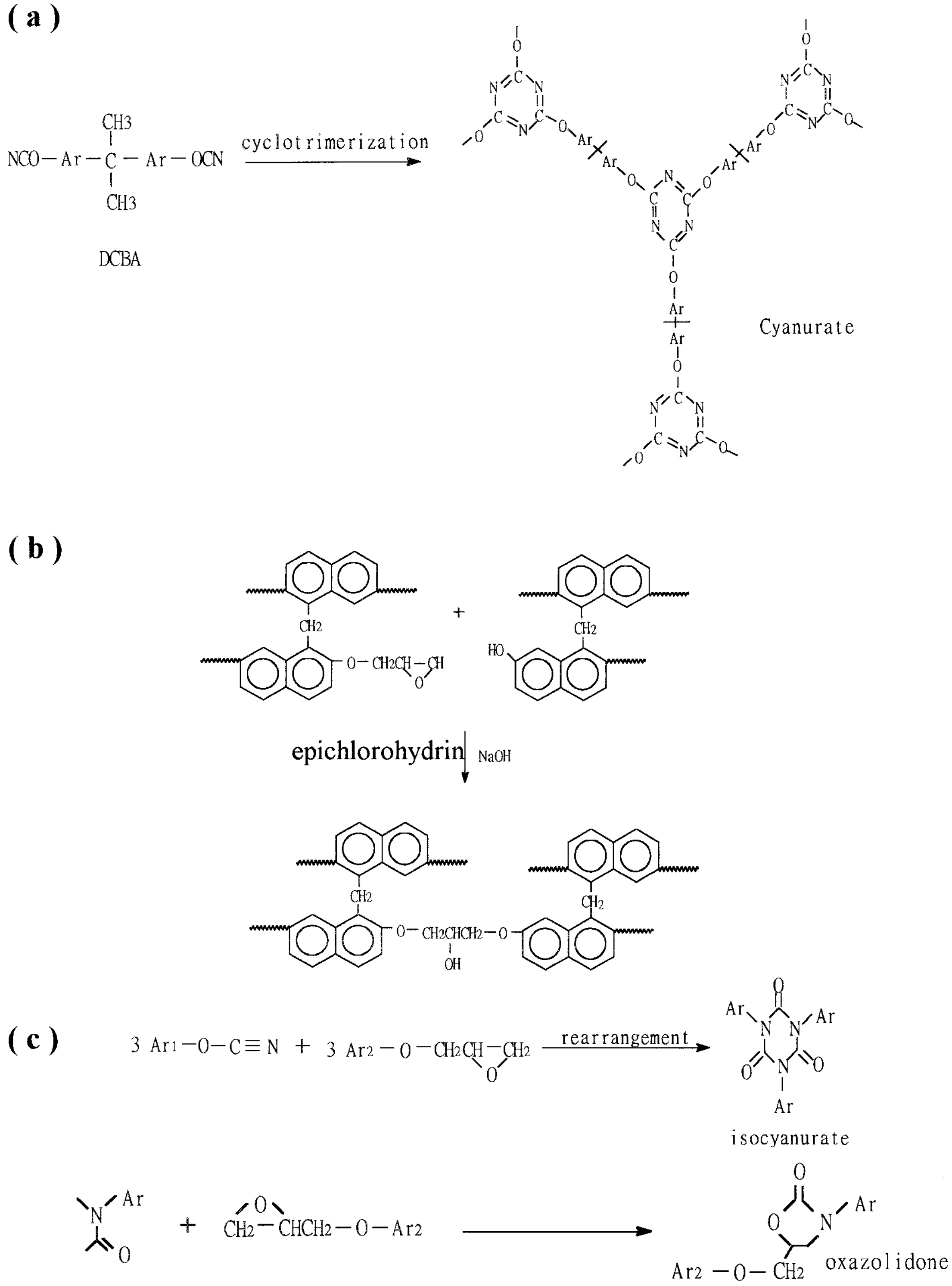
Figure 3 shows the changes in FTIR spectra when the dicyanate of bisphenol A (DCBA) was used to cure a typical tetrafunctional naphthalene-containing epoxy resin. Spectrum (1) shows two cyanate absorption peaks of DCBA at 2270 and 2235 $\mathrm{cm^{-1}}$ which are due to the —O—C≡N vibration absorption of DCBA. After DCBA was heated to 200°C for 4 h, new absorptions were observed at 3450, 1750, and 1565 $\mathrm{cm^{-1}}$ as shown in spectrum (2) and Figure 4(a). The band at 3450 $\mathrm{cm^{-1}}$ was due to N—H stretching; the band at 1750 $\mathrm{cm^{-1}}$ was due to C═O stretching[18]; and the peak at 1565 $\mathrm{cm^{-1}}$ was due to the triazine ring vibration. Spectrum (3) shows a peak at 915 $\mathrm{cm^{-1}}$ which is due to the epoxy group. A broad absorption at 3440 $\mathrm{cm^{-1}}$ indicates the presence of the hydroxyl group which formed during epoxidation [Fig. 4(b)]. The last spectrum, spectrum (4), exhibits a significant absorption at 1745 $\mathrm{cm^{-1}}$ for the carbonyl group of the isocyanurate or oxazolidone structure resulting from the reaction of glycidyl ether with the cyanate ester [Fig. 4(c)]. The triazine ring is also observed at 1565 $\mathrm{cm^{-1}}$ with a coincident decline in absorption at 2270 $\mathrm{cm^{-1}}$ for the O—C≡N group. Characteristic absorption of the hydroxyl group is also observed in spectrum (4). Two main reactions may consume this secondary hydroxyl group of the epoxy resin in the epoxy/cyanate ester system: One is epoxy–hydroxyl addition (esterification) and the other is cyanate–hydroxyl addition. The former reaction hardly occurs under this curing condition, which will be discussed later in the DSC analyses. The latter reaction will not occur under the stoichiometry employed here [imidocarbonate group absorption at 1670 $\mathrm{cm^{-1}}$ was not observed in spectrum (4) of Fig. 3]. The IR spectra of various epoxy/DCBA-cured thermosets are shown in Figure 5 and are summarized in Table II.

Thermal Stability Analyses

Thermal stability was assessed by thermogravimetric analysis (TGA). TGA curves are shown in Figures 6 and 7 and corresponding decomposition data are listed in Table III. The temperature corresponding to a 10% weight loss is a crude index of thermal stability.[19] Cured neat DCBA had the best thermal stability, which may be attributed to its crosslinking cyanurate structure which resists thermal decomposition. Within the naphthalene-containing epoxy series, the thermal stability increases with increasing functionality of the epoxy resins. In addition to cured neat DCBA being the most stable, the char yields at 800°C also increase with increasing functionality of the epoxy resins, which may be attributed to the crosslink density of the cured systems. Comparing the thermal stabilities of **II-5** cured with DCBA (functionality = 2) and with 4-4′-diaminodiphenylsulfone (DDS, functionality = 4) in Figure 6 and Table 3, the $T_{10\%}$ of DCBA-cured **II-5** was 17°C higher than that of DDS-cured **II-5**, and the maximum decomposition temperatures ($T_{\max}$) were 452°C versus 407°C, indicating better thermal stability for the DCBA-cured system than that of the DDS-cured system.

DSC Analyses

The thermal polymerization behavior of DCBA and epoxy resin/DCBA systems at a scan rate of 10°C/min was investigated and the results are depicted in Figure 8. Neat DCBA has a melting



(Ar_1 is the bisphenol moiety, Ar_2 is the naphthalene epoxy moiety, Ar is mixed moiety of Ar_1 and Ar_2)

Figure 4 (a) Cyclotrimerization of DCBA; (b) side reaction of 1,1′-bis(2,7-hydroxy-1-naphthyl)methane with epichlorohydrin under the effect of sodium hydroxide; (c) reaction of naphthalene-containing epoxy and DCBA.

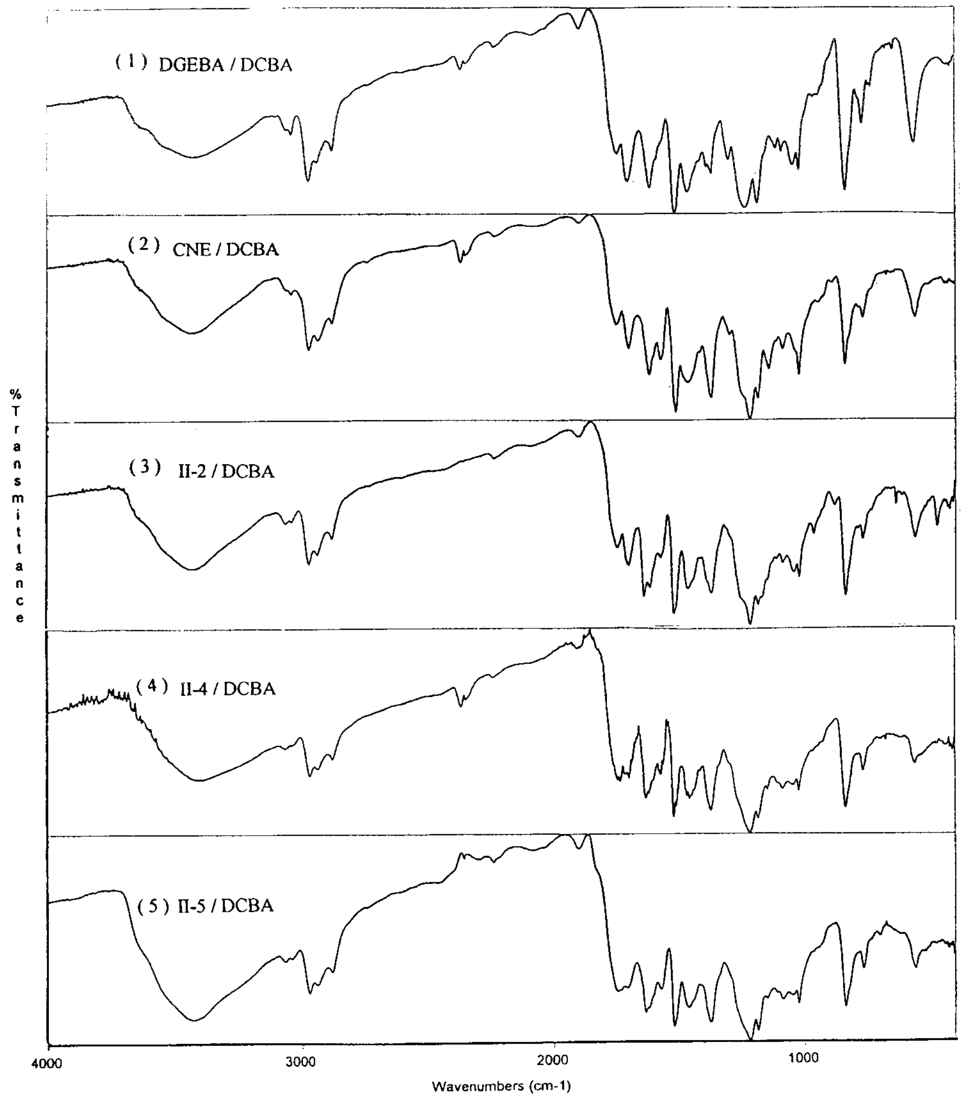


Figure 5 IR spectrum of various epoxy resins cured with DCBA: (1) DGEBA/DCBA, (2) *o*-cresol formaldehyde novolac epoxy (CNE)/DCBA, (3) **II-2**/DCBA, (4) **II-4**/DCBA, and (5) **II-5**/DCBA, all at the same molar ratio (oxirane group/cyanate group = 1/1.2) using a copper acetylacetonate/nonylphenol mixture as a catalyst, postcured at 200°C/4 h.

endotherm at about 76°C and an onset of exothermic homopolymerization temperature at about 135°C, reaching an exothermic peak maximum at about 230°C, with a processing window of 135–230°C and $\Delta H = 620$ J/g (curve 1). Cyanate ester may cure thermally or in the presence of transition-metal catalysts, such as the carboxylates of copper, cobalt, or zinc and an involatile phenol.[20] In this study, a catalyst mixture consisting of *p*-nonylphenol and copper acetylacetonate was used. The DSC scan of DCBA with the catalyst is depicted in curve 2 and did not show a melt endotherm because of overlapping of the trimerization exotherm and the melting endotherm. The exothermic peak maximum has shifted from 230°C to 101°C, indicating that the cyclotrimerization was greatly facilitated by the catalyst mixture. Curves 3 and 4 reveal two exothermic peaks similar to the phenomenon reported by Shimp et al.[21]

To understand the type of reactions happening in this region, a **II-5**/DCBA/catalyst mixture was analyzed at three intervals: Figure 9(1) reveals that cyclotrimerization (triazine ring absorption at 1565 cm^{-1}) started at the mixing temperature of 40°C with the catalyst mixture. The mixture

Table II IR Spectroscopic Characterization

Component	Absorption Band			
	ν Epoxy	ν Triazine	ν Oxazolidinone	ν OH
DGEBA	920	—	—	3504
CNE	920	—	—	3452
II-2	915	—	—	3452
II-4	915	—	—	3440
II-5	915	—	—	3456
DGEBA/DCBA	Invisible	1565	1745	3412
CNE/DCBA	Invisible	1565	1750	3428
II-2/DCBA	Invisible	1565	1739	3428
II-4/DCBA	Invisible	1565	1745	3436
II-5/DCBA	Invisible	1565	1745	3432

was heated to 130°C in the DSC oven with a scan rate of 10°C/min and then quickly cooled to room temperature and the IR spectrum [Fig. 9(2)] taken. Peak areas were calculated for the cyanate group at 2235 and 2270 cm^{-1}, the epoxy group at 915 cm^{-1}, the triazine ring at 1565 cm^{-1}, and the carbonyl group at 1745 cm^{-1}. The C—H stretching peak at 2950 cm^{-1} was used as the reference peak.[18] It showed decreases in the cyanate group and epoxy group absorptions and increases in triazine and carbonyl absorptions. When it was further heated to 280°C, Figure 9(3) shows that the cyanate group disappeared and the epoxy group becomes almost invisible, while the absorption of hydroxyl group increases.

The influence of the catalyst upon the naphthalene-containing epoxy resin **II-5** and **II-5**/DCBA are presented in curves 1 and 2 of Figure 10. In comparison with the uncatalyzed **II-5** epoxy resin (curve 1), the catalyzed **II-5** (curve 2) shows a lower exothermic onset temperature at 260°C due

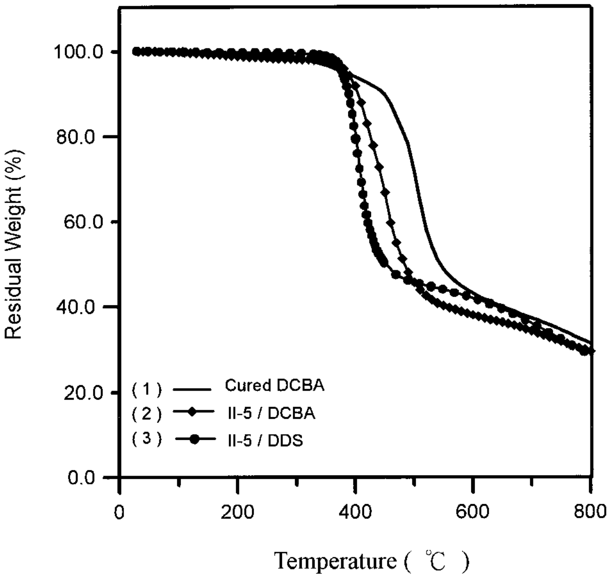


Figure 6 TGA thermograms of (1) cured neat DCBA, (2) **II-5** cured with DCBA (—O—C≡N/epoxy group = 1.2/1), and (3) **II-5** cured with 4-4′-diamodiphenylsulfone (DDS) (N—H/epoxy group = 1/1). All were postcured at 200°C/4 h.

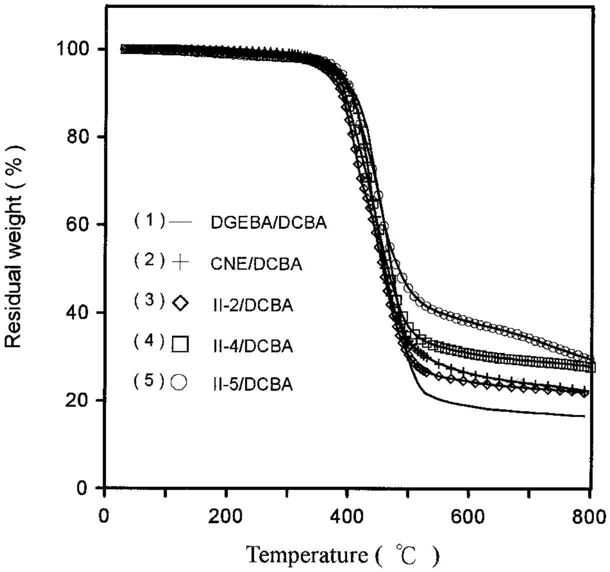


Figure 7 TGA thermograms of various epoxy resins cured with DCBA: (1) DGEBA, (2) CNE, (3) **II-2**, (4) **II-4**, and (5) **II-5**, all at the same molar ratio (oxirane group/cyanate group = 1/1.2) using a copper acetylacetonate/nonylphenol mixture as a catalyst, postcured at 200°C/4 h.

Table III Thermal Decomposition Properties of Various Epoxy Resins/DCBA-cured System

Component	$T_{10\%}$	T_{max}	Char Yield (800°C) (wt %)
Cured DCBA	446	500	31
DGEBA/DCBA	405	470	16
CNE/DCBA	403	452	22
II-2/DCBA	389	452	22
II-4/DCBA	393	454	27
II-5/DCBA	405	451	29
II-5/DDS	388	407	29

to either cationic polyetherification or coordination polyetherification of epoxide when a metallic catalyst was added.[22] Uncatalyzed **II-4** exhibited a similar tendency to uncatalyzed **II-5**, so the epoxy–hydroxyl addition has hardly occurred. The catalyst also played an important role in decreasing the activation energy of the **II-5**/DCBA reaction (curves 3 and 4 of Fig. 10). In curve 4, the integral area of first peak for the **II-5**/DCBA system (ΔH = 45 J/g) is smaller than that of the DGEBA/DCBA system (ΔH = 155 J/g), which is shown in Figure 10, curve 3. The multifunctional naphthalene-containing epoxy resin sterically hindered the approach of cyanate ester to form the cyanurate, which is the first step of cyanate ester/epoxy resin reaction,[12,20] and resulted in a smaller heat of reaction and an incomplete crosslinking reaction. This is why DGEBA/DCBA has a better thermal stability than that of **II-2**/DCBA.

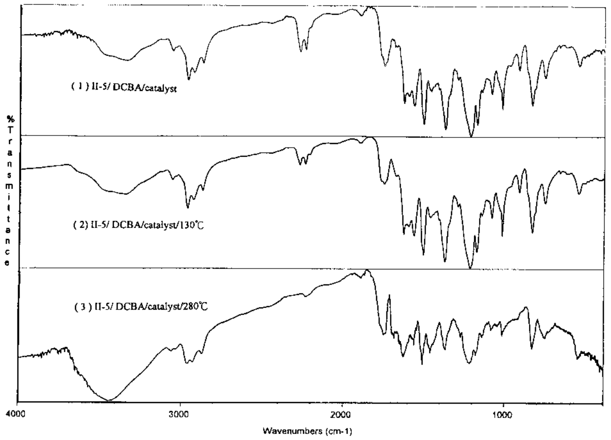


Figure 9 IR spectrum of (1) a **II-5**/DCBA/catalyst mixture at 40°C, (2) a **II-5**/DCBA/catalyst mixture heated to 130°C, and (3) **II-5**/DCBA/catalyst mixture heated to 280°C.

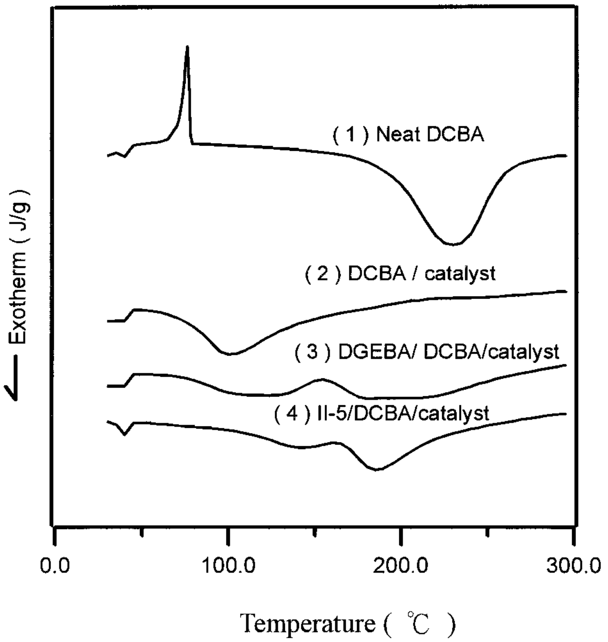


Figure 8 DSC thermograms of (1) uncatalyzed DCBA, (2) catalyzed DCBA, (3) DGEBA/DCBA/catalyst, and (4) **II-5**/DCBA/catalyst. All specimen were heated at a scanning rate of 10°C/min in nitrogen.

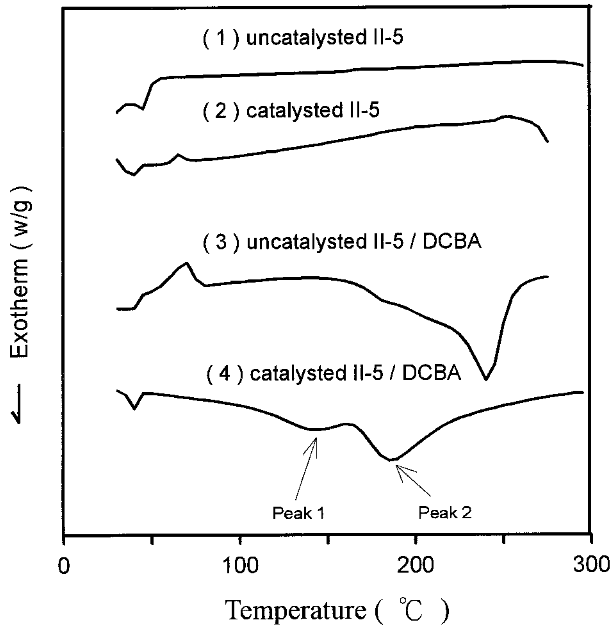


Figure 10 DSC thermograms of (1) uncatalyzed **II-5** epoxy resin, (2) catalyzed **II-5** epoxy resin, (3) uncatalyzed **II-5**/DCBA mixture, and (4) catalyzed **II-5**/DCBA mixture. All mixtures were heated at a scanning rate of 10°C/min in nitrogen.

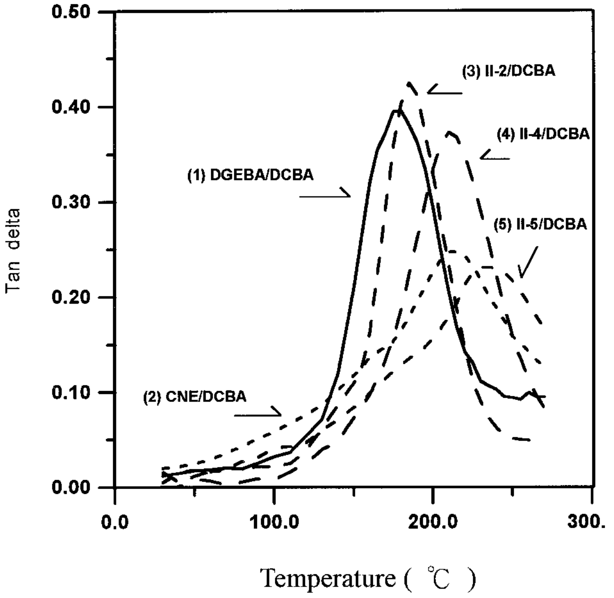


Figure 11 Dynamic mechanical thermograms of the thermosetting epoxy resins cured with DCBA: (1) DGEBA/DCBA, (2) CNE/DCBA, (3) **II-2**/DCBA, (4) **II-4**/DCBA, and (5) **II-5**/DCBA, all at the same molar ratio (oxirane group/cyanate group = 1/1.2) using a copper acetylacetonate/nonylphenol mixture as a catalyst, postcured at 200°C/4 h.

Dynamic Mechanical Analysis

Dynamic mechanical analysis can give us information on the microstructure of cured epoxy resins. The peak of the tan δ curve is referred to as the glass transition temperature and the results are shown in Figure 11. At 200°C postcure temperature, the difunctional epoxy resins including both DGEBA/DCBA and **II-2**/DCBA had a T_g below the oven temperature of 200°C, indicating that they had already achieved the ultimate T_g. Table IV shows that the DCBA-cured difunctional naphthalene-containing epoxy resin **II-2** has a higher T_g than that of DGEBA. The reasons for CNE/DCBA having a T_g 10°C higher than the curing temperature might be due to the curing exotherm of multifunctional CNE increasing the cure temperature above that of the oven temperature. In the naphthalene-containing series, the T_g increased with increase of the epoxy functionality.

Dimensional Stability Analyses

The CTE are presented in Table IV. The irregular molecular arrangement of the CNE resulted in a larger free volume and a lower density than that of the others and, hence, has the highest coefficient of thermal expansion. The CTE of the cured neat DCBA was the smallest and this is attributed to the cyclotrimerization of DCBA to form a crosslinked cyanurate network.

Moisture Absorption

The absorbed moisture in the semiconductor package and printed circuit board were found not only to plasticize the epoxy resin, causing a lowering of the T_g, but also to cause the package to crack during the soldering process.[23] As depicted in Table IV, for difunctional epoxy resins (DGEBA and **II-2**) cured with DCBA, the introduction of the naphthalene group into the backbone effectively depressed the moisture absorption, so **II-2**/DCBA has a better water-resistance property than that of DGEBA/DCBA. In the naphthalene-containing series, moisture absorption increased with the epoxy functionality, which may be attributed to a more polar oxazolidone structure formation for a higher functional epoxy compound.

CONCLUSIONS

Multifunctional epoxy resins containing a naphthalene backbone were synthesized by epoxida-

Table IV Physical Property Characterization

Component	ρ (g/cm^3)	α (ppm/°C)	% Water Absorption	T_g
Cured DCBA	1.2242	26.89	0.98	210
DGEBA/DCBA	1.2436	35.94	1.20	179
CNE/DCBA	1.2244	63.70	1.83	210
II-2/DCBA	1.2792	30.42	1.00	187
II-4/DCBA	1.2879	34.75	1.85	211
II-5/DCBA	1.2415	35.12	1.98	240

tion of the corresponding di-, tetra-, and pentafunctional novolacs with excess epichlorohydrin. The glass transition temperature, thermal stability, and moisture absorption were found to increase as the epoxy functionality increased. The onset reaction temperature of the epoxy with cyanate ester can be reduced by the addition of a metallic catalyst. **II-5**/DCBA exhibits a better thermal stability, indicating that multifunctional epoxy resins containing naphthalene cured with DCBA are suitable candidates for high-performance electronic application. A lower reaction heat release in the DSC scan for naphthalene-containing epoxy resins than for other commercial epoxy resin systems reveals that the naphthalene system has a higher steric hindrance.

REFERENCES

1. Fujita, H.; Mogi, N. IEEE 1993, 735.
2. Wang, C.-S.; Lee, M.-C. Polym Bull 1998, 40, 623.
3. Wang, C.-S.; Lee, M.-C. J Appl Polym Sci, in press.
4. Murayma, T.; Bell, J. P. Polym Sci Part A 1970, 2, 437.
5. Arridge, R. G.; Speake, J. H. Polymer 1970, 13, 443.
6. Keenan, J. D.; Seferis, J. C.; Quinlivan, J. T. J Appl Polym Sci 1979, 24, 2375.
7. Mijovic, J.; Willians, J. G.; Donnellan, T. J Appl Polym Sci 1985, 30, 2351.
8. Charesworth, J. M. Polym Eng Sci 1988, 28, 221.
9. Grillet, A. C.; Galy, J.; Gerard, J. F.; Pascault, J. P. Polymer 1991, 32, 1885.
10. Stutz, H.; Mertes, J. J. Polym Sci Part A Polym Chem Ed 1993, 31, 2031.
11. de Nogravo, F.; Guerrevo, P.; Corcuera, M. A.; Mondragon, I. J Appl Polym Sci 1995, 56, 177.
12. Bauer, J.; Bauer, M. J Macromol Sci Chem A 1990, 27, 97.
13. Bauer, J.; Bauer, M. Makromol Chem Macromol Symp 1989, 30, 1.
14. Kim, B. S. J Appl Polym Sci 1997, 65, 85.
15. Richard, B. G. Polym Prepr 1986, 27, 491.
16. Kubens, R.; Schulthier, H. U.S. Patent 3562214, 1971.
17. Schroeder, J. A.; Madsen, P. A.; Foister, R. T. Polymer 1987, 28, 929.
18. Owusu, A. O.; Martin, G. C.; Gotro, J. T. Polymer 1996, 37, 4869.
19. Snow, A. W.; Buckley, L. J. Macromolecules 1997, 30, 394.
20. Adam, C.; Ian, H. Macromolecules 1994, 27, 4927.
21. Shimp, D. A. In 37th International SAMPE Symposium and Exhibition, March 9–12, 1992; p 293.
22. Lin, S. C.; Pearce, E. M. High-performance Thermosets: Chemistry, Properties, Applications; Hanser/Gardner: Cincinnati, 1994.
23. Kimura, H.; Ohizumi, S.; Nishioka, I.; Nakao, M.; Horada, M. IEEE 1992, 1035.