

Synthesis, Characterization, and Curing Properties of Novel Phosphorus-Containing Naphthyl Epoxy Systems

Hao Ai,¹ Kai Xu,¹ Huan Liu,¹ Mingcai Chen,¹ Xiuju Zhang²

¹Key Laboratory of Polymer Materials for Electronics, Guangzhou Institute of Chemistry, Chinese Academy of Sciences, Guangzhou 510650, People's Republic of China

²Department of Materials Science and Engineering, Jinan University, Guangzhou 510632, People's Republic of China

Received 4 July 2008; accepted 23 January 2009

DOI 10.1002/app.30108

Published online 19 March 2009 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: In an attempt to obtain flame-retardant epoxy systems with high thermal properties, novel phosphorus-containing naphthyl epoxies were synthesized through the addition reaction of diethyl phosphite and two naphthyl epoxy monomers, diglycidyl ether of 2,2'-hydroxy-1,1'-binaphthalene and 1,1'-diglycidylidynaphthylmethane. The addition reaction was monitored with Fourier transform infrared spectroscopy and solubility experiments, and the reaction conditions were studied. The spectral results showed that oxirane in phosphorus-modified epoxies could undergo an isomerization process in which carbonyl groups were generated during the reaction at temperatures

higher than 140°C. The structure and epoxy equivalent weight of the modified naphthyl epoxies were determined by means of ¹H-NMR and ³¹P-NMR. The thermal curing reactivity and activation energy of the phosphorus-containing naphthyl epoxies were investigated with differential scanning calorimetry with dicyanodiamide and diaminodiphenylsulfone as the curing agents, and they were compared with those of an epoxy modified with 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 113: 541–546, 2009

Key words: curing of polymers; FT-IR

INTRODUCTION

Epoxy resins are widely used in the fields of coatings, adhesives, casting, potting, composites, lamination, and semiconductor device encapsulation because of their excellent adhesion, good mechanical and electrical properties, superior dimensional stability, and good resistance to heat and chemical attack.^{1,2} However, the poor flame retardancy of epoxy resins limits their usage; improving this property is desirable. To reduce the flammability of epoxy thermosets, inherently flame-retardant phosphorus-containing epoxy systems have been widely investigated in recent years.^{3–9}

Various organophosphorus groups can be covalently incorporated into the backbone of epoxy resins. For the class of phosphate-based epoxies, because of the inherent flexibility and poor stability of the P—O—C bond, the cured polymers usually exhibit a low glass-transition temperature and low thermal stability. In recent years, some epoxy derivatives have been synthesized from a bulky, rigid, phosphorus-containing, and reactive 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO).^{10–15} These aryl phosphine compounds have unusually

high thermal stability, which is attributable to the O=P—O group being protected by the phenylene groups.

The aim of this work is the presentation of a novel phosphorus-containing epoxy with improved thermal stability. It has been known that the incorporation of a naphthalene unit into polymeric systems makes a strong contribution to thermal stability because of its excellent rigidity and facile packing of molecules. Diethyl phosphite (DEP), like DOPO, bears a reactive P—H bond, which can undergo an addition reaction with an epoxy group. In our laboratory, phosphorus-containing naphthyl epoxies were synthesized via a prereaction between two naphthyl epoxy monomers and DEP. This reaction was monitored with Fourier transform infrared (FTIR) spectroscopy and solubility experiments in acetone. The structure and epoxy equivalent weight (EEW) of the modified naphthyl epoxies were determined by means of ¹H-NMR and ³¹P-NMR. In practice, the characterization of thermal curing behaviors is fundamental if the relationships between the structure and properties are to be understood. The curing behavior and activation energy (E_a) provide information about what the processing conditions should be to meet the requirements of their end use. We examined the curing reaction of phosphorus-modified epoxies with differential scanning calorimetry (DSC), using two amino curing agents,

Correspondence to: K. Xu (xk@gic.ac.cn).

dicyanodiamide (DICY) and diaminodiphenylsulfone (DDS); the curing behaviors were compared with that of a DDS/DOPO-modified diglycidyl ether of 2,2'-hydroxyl-1,1'-binaphthalene (DGEBN) curing system.

EXPERIMENTAL

Materials

DGEBN (EEW = 205 g/equiv) and 1,1'-diglycidylidene naphthylmethane (EN; EEW = 212 g/equiv) were prepared by procedures described in previous articles.^{16,17} Diglycidyl ether of bisphenol A (EPON828; EEW = 188 g/equiv) was obtained from Shell Chemical Co. (New Milford, Connecticut) DEP (98%; Fluka, Switzerland), DOPO (TCI, Japan, Burma), DICY (99%; Aldrich, United States), DDS, ethylene glycol monomethyl ether, and triphenylphosphine (purchased from Chemical Reagent Co., Shanghai, China) were used without further purification.

Synthesis of the phosphorus-containing epoxies

A typical synthetic route toward a DEP-modified naphthyl epoxy was as follows, with DGEBN(P2) used as an example. Into a four-necked, round-bottom flask equipped with a nitrogen inlet, stirrer, and temperature controller were added 0.5 mol of DGEBN (102.5 g) and 0.075 mol of DEP (10.4 g). The reaction mixture was gradually heated to 140°C. Thereafter, 0.6 mg of ethyl triphenylphosphine was added gradually, and the mixture was maintained at 140°C for 4 h. A solubility experiment using acetone and FTIR spectra were used to observe the progress of the reaction. When the P—H bond vibration absorption peak (2430 cm^{-1}) disappeared, the reaction was ended by the cooling of the reaction mixture. Then, $^1\text{H-NMR}$ was used to evaluate the EEW values of the phosphorus-containing epoxy oligomers.

DOPO-modified DGEBN was prepared according to a published procedure.¹⁸

Preparation of the curing systems

The modified epoxies and curing agents in a molar stoichiometric ratio of 1 : 1 were dissolved in a mixed solvent of acetone, ethylene glycol monomethyl ether, and dimethylformamide. The solvent was evaporated *in vacuo*. The samples were kept in a refrigerator before the DSC experiment.

Characterization

NMR ($^1\text{H-NMR}$ and $^{31}\text{P-NMR}$) spectra were obtained on a DRX 400 apparatus from Bruker (Fällanden, Switzerland) with CDCl_3 as a solvent. The $^1\text{H-NMR}$ and $^{31}\text{P-NMR}$ spectra were referenced to

tetramethylsilane and 85% orthophosphoric acid, respectively. FTIR spectra were recorded with an RFX-65A infrared spectrometer (Beijing, China). The EEWs of the phosphorus-containing epoxies were evaluated with NMR spectroscopy at 27°C.

DSC was used to determine the curing behavior. The measurement was carried out with a TA-DSC2010 (New Castle, Delaware) instrument under a nitrogen atmosphere. The curing system was heated from 25 to 270°C at a heating rate of 20°C/min. The exothermic peak during curing was identified by the peak temperature and onset temperature (T_o).

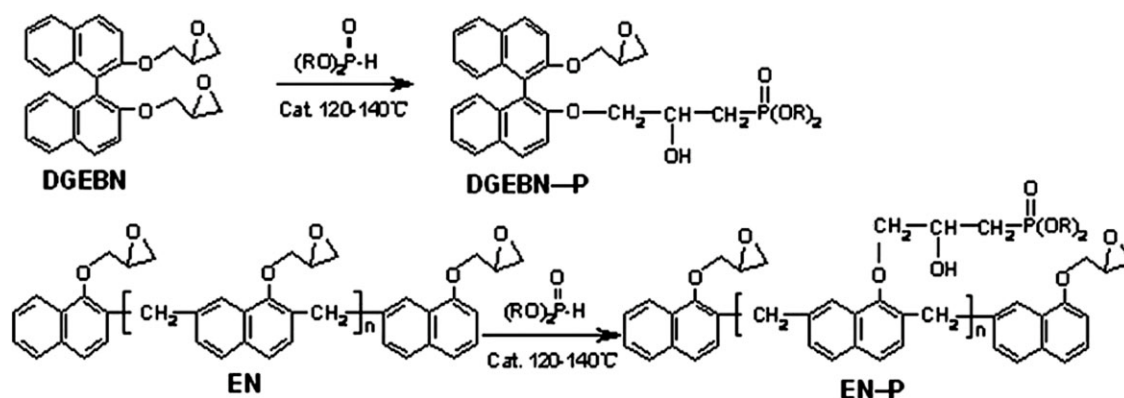
RESULTS AND DISCUSSION

Synthesis and characterization

In the DEP molecule, there is an active hydrogen atom (P—H) that can react with double bonds such as C=C and C=N. According to the published literature,^{19,20} the P—H bond can undergo an addition reaction with electron-deficient carbon in the oxirane skeleton and generate P—C bonds under certain conditions. The synthesis method for organophosphorus-modified epoxy oligomers via a ring-opening addition reaction of naphthyl epoxies with DEP is summarized in Scheme 1.

Through changes in the molar ratio of epoxy to DEP, a series of epoxy oligomers with different phosphorus contents were obtained. Secondary hydroxyl —OH groups were generated during the addition reaction. The generated —OH group in turn could undergo etherification reactions with other epoxy groups or undergo dealcoholization reactions with ethoxy groups in DEP molecules. These reactions could result in an unexpected occurrence of gelation. In addition, the existence of DEP could lead to an isomerization process of epoxy groups and then increase the EEW, thus exerting an undesirable influence on the curing behavior.

The addition reaction of DEP and epoxy was carried out in the presence of a quaternary phosphonium catalyst within the temperature range of 120–160°C. The FTIR technique was used to trace the progress of the modification. On the basis of the changes in the peak at 2430 cm^{-1} , which was attributed to the absorption of the P—H group, and the changes in the epoxy vibration peaks, the degree of conversion could be obtained. At 120°C both the epoxy group and P—H group exhibited slight changes in the absorption intensity after 6 h, and this indicated that the addition reaction of DEP and epoxies experienced a low rate under this condition. However, as shown in Figures 1 and 2, at temperatures up to 140°C, changes in the peak absorption became evident. Epoxy groups in DGEBN and EN showed partial conversion, and the P—H peak absorption



Scheme 1 Schematic routes for preparing phosphorus-containing epoxies.

disappeared after 4 h when the molar ratio of DEP to epoxy monomers was below 0.5. This result showed the full conversion of DEP under the reaction conditions. On the other hand, a solubility experiment was performed to examine whether gelation of the reaction mixture could occur at an elevated temperature. It was an indication of no gelation when the synthesized phosphorus-containing naphthyl epoxies exhibited good solubility in acetone.

When the temperature was elevated further, some isomerization could occur during the addition procedure. Figures 3 and 4 illustrate the evidence and the probable route of the isomerization of the DGEBN-DEP and EN-DEP systems, respectively. When the temperature was elevated up to 160°C , the intensities of the P-H absorption peak and epoxy group absorption peaks decreased significantly along with the process, and they disappeared nearly entirely after 3 h of reaction. Simultaneously, new peaks were observed at 1708 and 1706 cm^{-1} in the DGEBN-DEP and EN-DEP systems, respectively. This was probably due to the absorption of the carbonyl group. The result leads us to conclude that together with

the addition reaction, an isomerization process takes place in the modification process for both DGEBN and EN. This is shown in Figures 3 and 4. The isomerization reaction is presumably related to the P-H group, although the mechanism involved is still not clear. A similar result has been reported in the literature: the phosphoryl group, acting as a nucleophile, can be involved in the isomerization of epoxides.²¹ As shown in FTIR spectra, this isomerization is a nonreversible reaction. The isomerization of the epoxy group into a carbonyl group in the reaction mixtures (the DGEBN-P and EN-P systems) may exhaust reactive groups (epoxy groups). Therefore, a further curing reaction of the naphthyl epoxies and curing agent would not proceed.

Because of the partial consumption of epoxy groups by P-H, EEWs of the modified products would increase. By comparing the changes in EEW, we can also evaluate the progress of the reactions. However, an evaluation of EEW by hydrochloric acid/acetone titration methods in this work may be difficult to achieve. The titration method is based on the yielding of the ring-opened epoxy under acidic conditions. This will probably result in wrongly determined EEW values because P-O-C₂H₅ would spontaneously hydrolyze into P-OH during titration and then make a contribution to the consumption of the base (NaOH). Therefore, this method is not

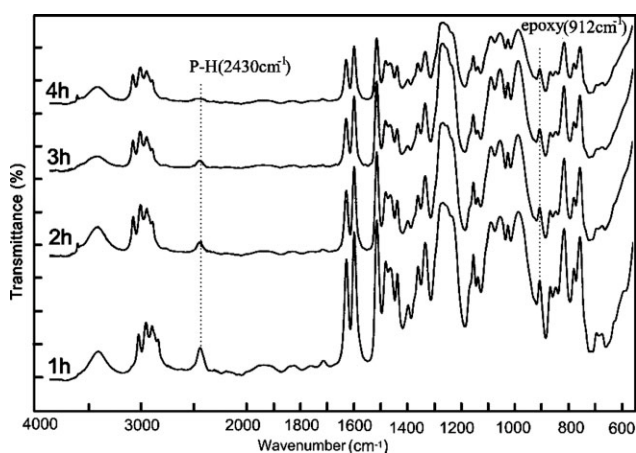


Figure 1 FTIR spectra recorded from DGEBN-DEP (1 : 0.5 mol) at different times at 140°C .

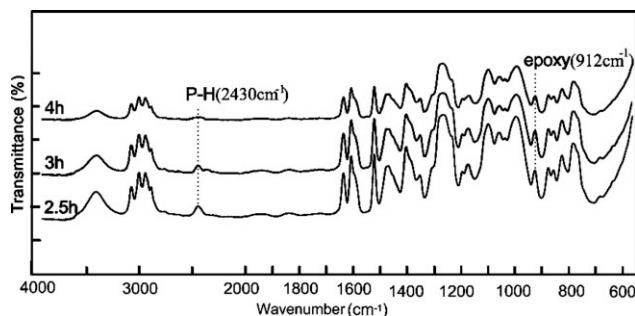


Figure 2 FTIR spectra recorded from EN-DEP (1 : 0.5 mol) at different times at 140°C .

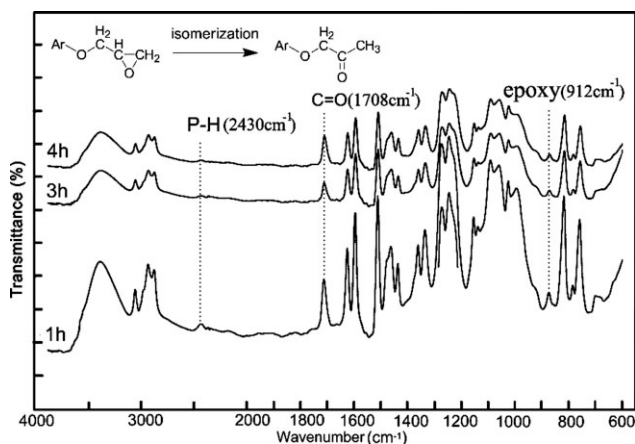


Figure 3 Changes in the FTIR spectra with time for DGEBN-DEP (1 : 0.5 mol) at 160°C.

applicable for determining EEW. The NMR technique offers an alternative method for EEW evaluation. The $^1\text{H-NMR}$ spectra of modified epoxies were recorded with 1,1,2,2-tetrachloroethane (TCE; $\delta = 5.9$ ppm) as the reference compound. Comparing the intensity of the methylene peak ($\delta = 2.25, 2.47$ ppm) in the epoxy group to that of TCE, we could evaluate EEW without the interference of hydrolysis. The values of EEW were determined with the following equation:

$$\text{EEW} = [(I_{\text{TCE}} \times m_{\text{epoxy}}) / (I_{\text{epoxy}} \times m_{\text{TCE}})] \times M_{\text{TCE}}$$

where I is the integral intensity of the proton peaks, M_{TCE} is the molecular weight of TCE, and m is the moles of samples. Table I summarizes the EEWs of the samples prepared in this work on the basis of NMR spectroscopy and their calculated values based on the molar contents of the DEP and epoxy monomers in the samples. The results from the NMR evaluation were in good agreement with those obtained from calculations.

With DGEBN(P2) as an example, the chemical structure of the modified epoxies was characterized with $^1\text{H-NMR}$ [Fig. 5(a)] and $^{31}\text{P-NMR}$ [Fig. 5(b)] spectroscopy. In Figure 5(a), the chemical shifts of

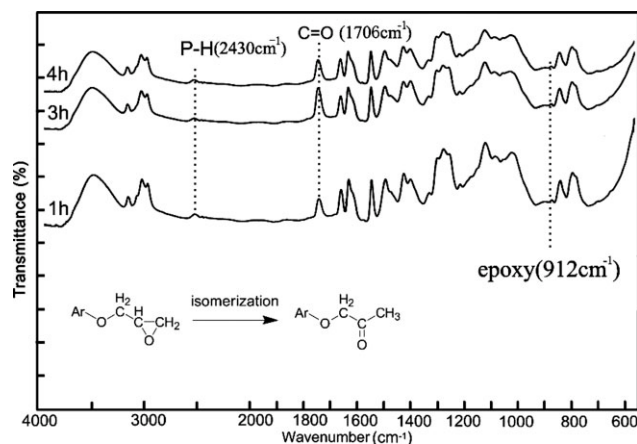


Figure 4 Changes in the FTIR spectra with time for EN-DEP (1 : 0.5 mol) at 160°C.

the aromatic protons ($-\text{C}_{10}\text{H}_6$) can be observed at 6.8–8.2 ppm (12H). The peaks at 4.1 (4H) and 2.8 ppm (4H) were assigned to the protons for $\text{C}_{10}\text{H}_6-\text{O}-\text{CH}_2-$ and $-\text{CH}_2$ in the oxirane ring. The peaks for the protons of $-\text{CH}$ in the oxirane ring overlapped with that of $-\text{CH}_2$ in the ethoxy groups of the DEP molecule, which appeared at 3.6–3.8 ppm (4H). The signals for the protons of $-\text{CH}_3$ in the DEP molecule appeared at 1.2 ppm (3H). The integral intensities of the protons were consistent with the calculated values from the proposed structure. The characteristic peak at 9.24 ppm in $^{31}\text{P-NMR}$ indicated the single chemical environment of phosphorus. This evidence strongly supports the proposed structure of the phosphorus-modified naphthyl epoxies.

Curing behavior of the phosphorus-containing epoxy systems

Dynamic DSC was used to investigate the thermal curing behavior of organophosphorus-modified epoxy systems using DDS or DICY as the curing agent. The data from dynamic DSC measurements at different heating rates were analyzed with the Kissinger method.²²

TABLE I
Compositions and EEW Data for the Samples

Sample	DGEBN : DEP (molar ratio)	P content (wt %)	EEW of the product	
			Theoretical	NMR method
EN(P5)	1 : 0.5	5.40	521	527
EN(P4)	1 : 0.35	4.05	410	419
EN(P3)	1 : 0.25	3.0	329	334
EN(P2)	1 : 0.15	1.94	278	281
DGEBN(P5)	1 : 0.5	5.71	506	514
DGEBN(P4)	1 : 0.35	4.21	390	402
DGEBN(P3)	1 : 0.25	3.10	310	315
DGEBN(P2)	1 : 0.15	2.02	257	260

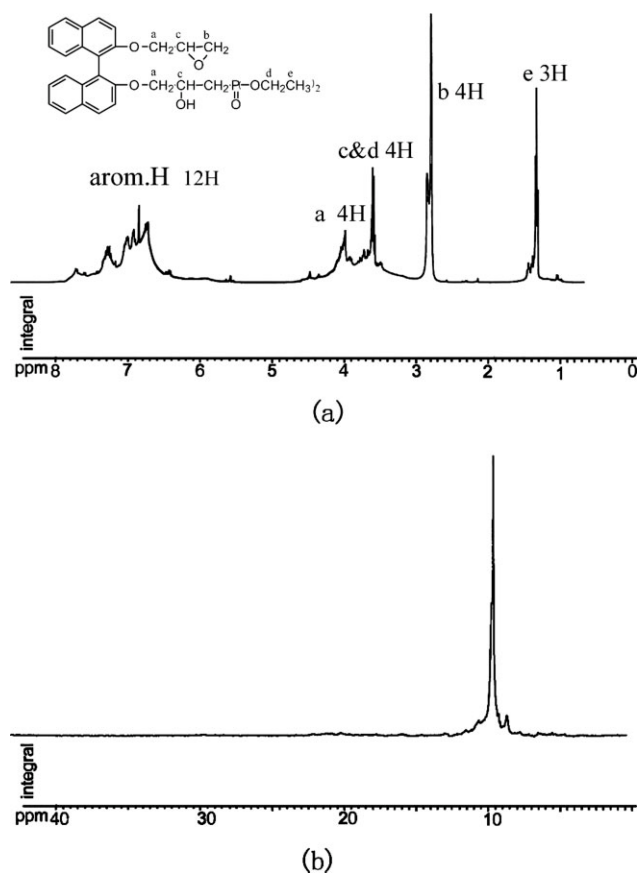


Figure 5 (a) ¹H-NMR and (b) ³¹P-NMR spectra of DGEBN(P4).

$$d[\ln(\beta/T_p^2)]/d(1/T_p) = -E_a/R$$

where β is the heating rate, T_p is the peak exotherm temperature, and R is the gas constant. E_a can be calculated from the slope of the plot. Figures 6 and 7 show the dynamic DSC thermograms for EN(P2)/DICY and EN(P2)/DDS curing systems (5, 10, 15, and 20°C/min). In each curve, an exothermic peak can be observed, and there is no endothermic peak.

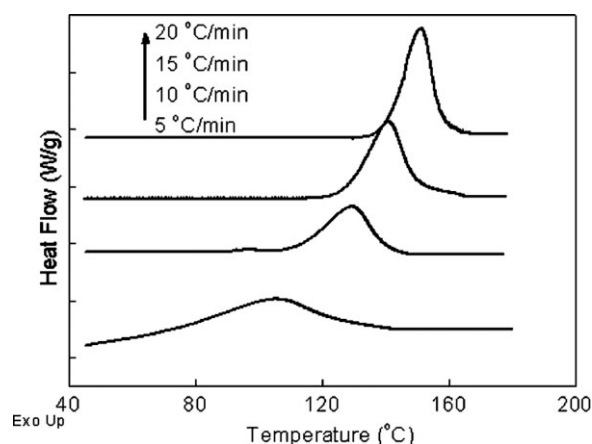


Figure 6 Dynamic DSC thermograms for the EN(P2)/DICY curing system.

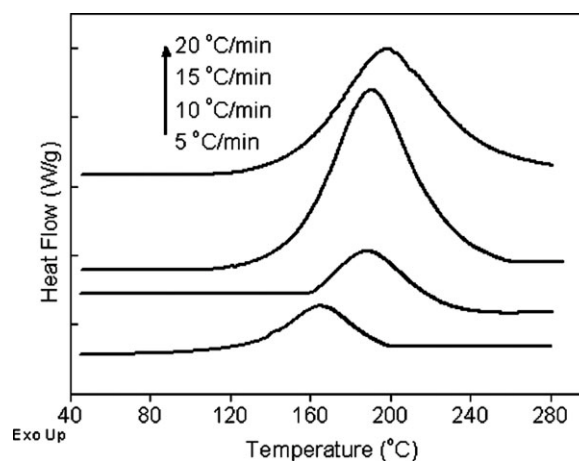


Figure 7 Dynamic DSC thermograms for the EN(P2)/DDS curing system.

The values for E_a , T_o , and the temperature of the maximum exothermic rate (T_m) are summarized in Table II. Data from the table indicate that the curing systems of the modified DGEBN and EN display a large reduction in T_o and T_m values in comparison with the unmodified epoxy monomers when cured with DDS or DICY. For the curing systems using DDS or DICY as a hardener, the T_o and T_m values for the modified naphthyl epoxies decreased with increasing phosphorus content. In the case of DDS, E_a decreased with increasing phosphorus content, whereas for DICY, E_a changed slightly with the phosphorus content. These results suggest that the reactivity of the modified naphthyl epoxies to amine is increased by the introduction of phosphorus. As mentioned previously, the EEWs of the modified epoxies increased with the phosphorus contents. This means that the functional group spatial density and the molecular mobility of the epoxy component were lowered by the introduction of phosphorus. Generally, the reactivity of the involved nucleophilic

TABLE II
Curing Parameters Obtained by DSC Measurements
(10°C/min) for Various Epoxy Systems

Sample	T_o (°C)	T_m (°C)	ΔH (J/g)	E_a (kJ/mol)
DGEBN(P2)/DDS	162.9	178.5	85.7	136.7
DGEBN(P3)/DDS	159.6	189.8	42.9	88.2
DGEBN(P4)/DDS	149.0	204.1	44.6	72.3
DGEBN/DDS	185.4	212.8	42.9	157.9
DGEBN(P2)/DICY	89.6	129.5	34.6	30.8
DGEBN(P3)/DICY	81.7	123.0	32.6	29.3
DGEBN(P4)/DICY	75.5	101.9	38.5	33.0
DGEBN/DICY	143.1	175.7	30.1	90.6
EN(P2)/DDS	167.5	183.4	59.2	79.9
EN(P2)/DICY	91.9	133.1	33.1	53.7
EN/DDS	205.3	224.6	52.5	100.1
EN/DICY	166.4	186.3	65.3	66.6
DGEBN(DOPO)/DDS	184.2	210.4	109.6	74.6

ΔH , change of enthalpy in the transition.

addition is related to the steric hindrance and resonance nature of the epoxy monomer structure. On the basis of these considerations, the modified naphthyl epoxies should display a lower reactivity than the unmodified monomers, and the reactivity decreases with an increase in the phosphorus content. Obviously, these considerations cannot reasonably interpret the experimental observations. It is known that the presence of hydroxyl-containing compounds (alcohols or alcohol species) considerably promotes the interaction of epoxy compounds with amines and other nucleophilic attack.^{23–26} Taking into account the promotion effect of hydroxyl groups for the curing reaction, an explanation consistent with the experimental observations could be obtained. The hydroxyl groups generated by the addition reaction of P–H and epoxies facilitated the ring opening of oxirane groups through the formation of hydrogen bonding; therefore, it is reasonable to expect a decrease in the E_a value of the curing reaction in comparison with the case in which no hydroxyl was generated for the unmodified epoxy. In a similar manner, the increase in the phosphorus content would increase the number of hydroxyl groups, resulting in a high reactivity of epoxies toward amine. A similar suggestion was reported by Wang and Lin.²⁷

On the other hand, modified EN exhibited lower reactivity toward DICY with high values of T_o , T_m , and E_a in comparison with the modified DGEBN. This was probably due to the positive substitution effect of extended conjugation in the DGEBN molecule, as described in our previous report.¹⁷ Comparing the T_o and T_m values of the DGEBN(P3)/DDS system and DGEBN(DOPO)/DDS system, we can conclude that the DEP-modified epoxy displays higher reactivity than the DOPO-modified epoxy. This may be attributable to the fact that DOPO blocks the reactivity of the epoxy. Additionally, a comparison of reactivities of amine groups was made. As shown in Table II, DDS displayed lower reactivity than DICY. This was probably due to the lower stability and nucleophilicity of the amine groups afforded by the electron-withdrawing $-\text{SO}_2-$ group. This influence has been discussed in detail by many researchers.^{23,28}

CONCLUSIONS

A series of phosphorus-containing naphthyl epoxies were synthesized by the addition reaction of naphthyl epoxy monomers with DEP. The processes were traced and investigated with FTIR, and the reaction conditions were examined. The curing behavior of epoxies modified with DDS and DICY were investigated with dynamic DSC experiments. The addition reaction conditions should be controlled strictly to

avoid the occurrence of an isomerization reaction, which would influence the curing behavior. The reactivity of phosphorus-containing epoxies toward DDS increases with increasing phosphorus content, but the phosphorus content does not significantly affect the E_a value of epoxies when DICY is used as a curing agent. The presence of $-\text{OH}$ groups is responsible for the promoted reactivity of the modified epoxies. The reactivity of modified epoxies cured with DICY is superior to the reactivity of modified epoxies cured with DDS. Systematic studies are in progress on the relationship between the incorporation of phosphorus and properties such as the thermal stability, viscoelasticity, and flame retardancy. It is reasonable to expect organophosphorus-modified naphthyl epoxies to have improved flame-retardant properties as well as excellent thermal stability. Detailed results will be presented elsewhere.

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