

Studies on Curing Kinetics and Total Thermal Degradation of the Modified Epoxy Copolymer with Penta-Coordinated Phosphate as a Tribranched Junction

JUNG-FONG LIN, CHING-FU HO, STEVE K. HUANG

Department of Chemical Engineering, National Taiwan University of Science and Technology, Taipei, Taiwan 106

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ABSTRACT: Curing kinetics and thermal degradation of phosphate-modified thiodiphenol-containing epoxy copolymer (P3-ETP) were conducted. The kinetic study reveals that P3-ETP resin has better curing properties than unmodified epoxy resin (ETP). The activation energy, in kJ/mol, was 61.5 for P3-ETP, 89.1 for ETP, 109.9 for Epon 1001, and 124.7 for Epon 828, respectively. The low activation energy of P3-ETP may indicate that the penta-coordinated phosphate moieties facilitated the self-crosslinking process by providing the needed flexibility of the epoxy backbone. Thermal degradation study reveals that the char yield at 850°C was 33.0% for P3-ETP, 24.8% for P3-EBPA, and 8.9% for E-1001 under nitrogen atmosphere. The thermal transformation of the phosphate moiety in P3-ETP into phosphate salt was confirmed by the presence of P and S elements in the char residue by scanning electronic microscope/energy dispersive X-ray and by the observation on the delaying emission of the thermal degradative volatiles in the Direct pyrolysis–gas chromatography/mass spectrometric analysis. The flame retardancy of the phosphate moieties with thiodiphenol (TDP) as a whole was found effective, judging from the char yield. This may imply that sulfur atom in TDP also providing additional thermal stability for the P3-ETP epoxy copolymer. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 77: 719–732, 2000

Key words: phosphate-modified thiodiphenol-containing epoxy copolymer; scanning electronic microscope/energy dispersive X-ray; thermal degradative volatiles; nonflammability; direct pyrolysis–gas chromatography/mass spectroscopy

INTRODUCTION

One of the characteristics of epoxy resins is the dimensional stability. The rigidity of the network, which often gives rise to brittleness results from the self-crosslinking in the thermal curing process,¹ thus limits the applications. As a consequence of this, a toughening agent such as carboxyl terminated butadiene acrylonitrile (CTBN) rubber^{2,3} among others^{1,4,5} is often used to soften the rigidity of the matrix. Some interpolymers⁶ of

ethylene-styrene that possess the rubbery characteristics in the ambient temperature and some blends⁷ of bisphenol A-polycarbonate/acrylonitrile–butadiene–styrene (ABS) provided the improvement in the impact properties of thermoplastics, and others such as structured latex^{8,9} could be the candidates for the use as toughening materials comparable with the CTBN. Toughening agent often is administrated by blending in the epoxy formulation. However, blending process may be governed by many factors and may depend on the state of art. An effective method of the improvement on the flexibility of the epoxy matrix may lie on the modification on the epoxy backbone. Copolymerization is one of the methods

Correspondence to: S. K. Huang.

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that has been shown the improvement on the flexibility, either through side-chain modification with the polymethylphenyl siloxanes^{10–12} or with main-chain modification with flexible segments.^{13–15} The present approach in this line of research is to carry out the modification with the penta-coordinated organophosphate group in the epoxy main chain. The immediate advantage of the phosphate-modified epoxy resin is the improvement on the flame resistance, a needed property but often lacking in the epoxy resins. It may also be envisaged that the incorporation of a penta-coordinated phosphate group may serve as a tribranching center with the thermally stable aryl moiety in the form of tris-thiodiphenolic branches. As the result, it may open the epoxy matrix and provides the needed flexibility that softens the otherwise tight and rigid epoxy matrix.

The aims of this study were to investigate the curing behavior and the degradative properties of the synthesized epoxy resin, which was modified with an organophosphate as a tribranched center in the epoxy backbone. The thermal degradation study includes the measurement of the char yield for the calculation of the limiting oxygen index (LOI).¹⁶ The examination on the residue content by scanning electronic microscope/energy dispersive X-ray (SEM/EDX) spectrometer and the detection of the thermal degradative volatiles (TDVs) by direct pyrolysis–gas chromatography/mass spectrometer (DP-GC/MS) were conducted to obtain information needed for the understanding of the thermal degradative process.

EXPERIMENTAL

Materials

Phosphorus oxychloride from Riedel-de Haën, triethylamine from Acros Chemical Co. and 4,4'-thiodiphenol (TDP) from Aldrich Chemical Co., Inc., were purchased locally. Bisphenol A (BPA) was supplied by Nan Ya Plastic Corp. 2,4,6-Tris(dimethylaminomethyl) phenol (DMP-30) from Anchor Chemical Co. was used directly.

Instrument Analysis

A BIO RAD FTS-40 spectrophotometer was used to obtain the IR spectra. Phosphate-modified copolymer was dissolved in appropriate solvent, then cast on NaCl plate. Bruker AM-300 WB FT-NMR was

used for the ¹H-NMR and ¹³C-NMR measurements. The differential scanning calorimetry (DSC) measurement was carried out by Du Pont 9000 Thermal Analyzer coupled with a TA 2000 data analysis system. Thermal degradation measurement was performed by the thermogravimetric analyzer of Perkin Elmer TGS-2. The CAMSCAN scanning electron series 4 with EDISUN GENESIS energy dispersive X-ray analyzer was used for the SEM/EDX measurement. Perkin-Elmer Turbo GC/MS spectrometer equipped with pyrolysis CDS 1000 was used for the measurement of thermal degradative volatiles of phosphonate-modified and unmodified samples.

Preparation of the Phosphate-Containing 4,4'-Thiodiphenol (P3-TDP)

To a 500 mL three-neck round-bottom flask equipped with a mechanical stirrer and thermometer, 65.4 g (0.3 mole) of TDP in 150 mL 2-methoxyethyl ether and 40 g (0.4 mole) of triethylamine were added. The amount of 19.4 g (0.1 mole) of phosphorus oxychloride was added slowly, and then the reaction mixture was heated after the addition. The reaction was then refluxed for 18 h. The reaction mixture was cooled and poured into water, and the product was extracted by chloroform. The P3-TDP was used directly after the solvent was removed.

P3-BPA was prepared according to the above procedures except BPA was substituted for the TDP.

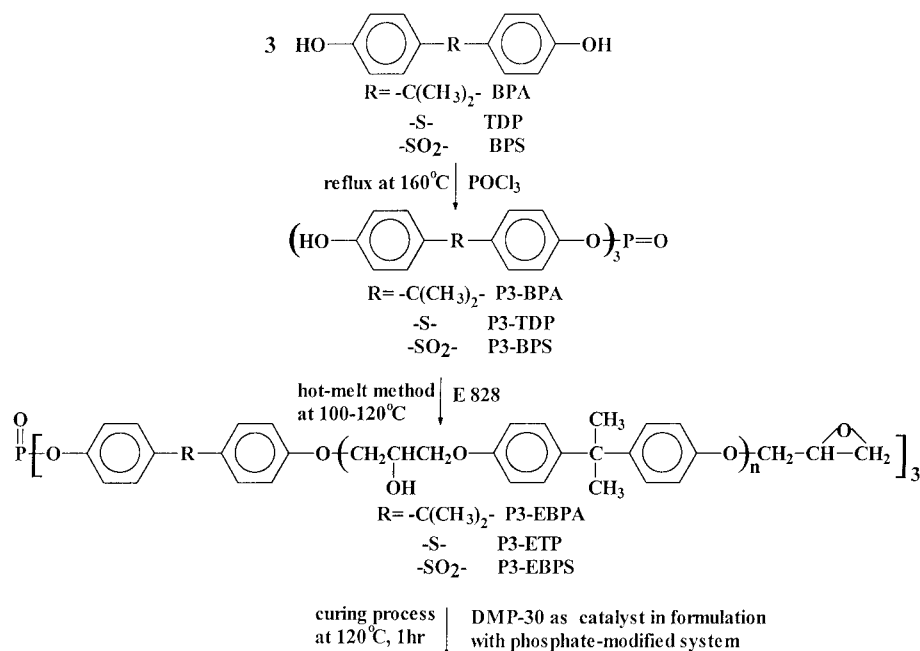
Preparation of the Phosphate-Modified 4,4'-Thiodiphenol-Containing Epoxy Copolymer (P3-ETP)

P3-ETP epoxy copolymer was prepared with the hot melt method with a ratio 1 : 3 of P3-TDP and Epon 828 at 100°C under N₂ atmosphere for 3 h.

P3-EBPA epoxy copolymer was prepared according to the hot melt method as described for P3-ETP, except P3-BPA was substituted for the P3-TDP.

Curing Kinetic Measurement of the P3-ETP Epoxy Copolymer

A sample of 5 mg of P3-ETP epoxy copolymer was weighed and placed in a DSC sample holder and sealed. The dynamic mode of the DSC measurement was carried out by a Du Pont 9000 Thermal Analyzer with the heating rate of 2.5, 5.0, 10, and 20°C/min under the flow of nitrogen with temper-



Testing of the specimens

Scheme 1 Preparation and curing process of phosphate-modified epoxy copolymers.

ature range from ambient to 250°C. The DSC thermogram was analyzed with TA 2000 data analysis system.

Thermal Degradation Study of the P3-ETP Epoxy Copolymer

A thermogravimetric analyzer of Perkin Elmer TGS-2 was used for the thermal degradation measurement. A sample of 5–8 mg was weighed accurately and placed in the sample holder. A heating rate of 20°C/min was used in the degradation study from ambient to 850°C under nitrogen and air atmosphere, respectively.

The Infrared Spectrum and the SEM/EDX Analysis of the Residue from Thermal Gravimetric Analysis (TGA) Measurement

The black char residue from TGA measurement under nitrogen was analyzed by a BIO RAD FTS-40 spectrophotometer to obtain the infrared data. The SEM/EDX measurement on the black residue was carried out by a CAMSCAN scanning electron series 4 with EDISUN GENESIS energy dispersive X-ray analyzer.

Thermal Degradative Volatile Measurement of the P3-ETP Epoxy Copolymer

TDVs were studied by the DP-GC/MS technique. Perkin-Elmer Turbo GC/MS spectrometer equipped

with CDS 1000 was used for the measurement. Pyrolysis was carried out by using the direct insertion probe for solid polymeric samples. A series of pyrolytic temperatures of 350, 400, 450, 500, and 900°C was selected for the measurement with the heating rate of 10°C/ms was used. The GC temperature program of 12°C/min from 80°C to the set temperature was carried out. The electric impact of 70 eV for the mass range of 0–600 was used.

RESULTS AND DISCUSSION

Synthesis and Structural Identifications

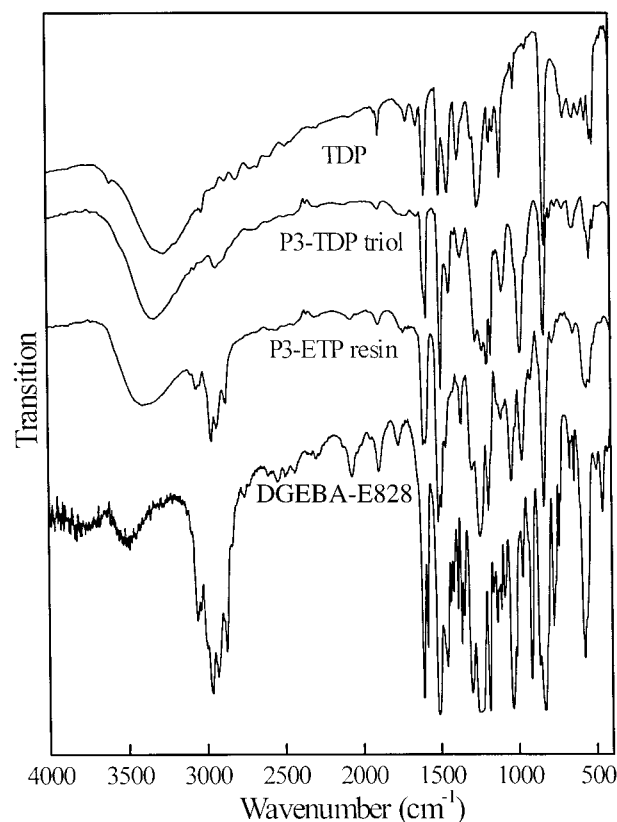
The preparation and the curing procedure for the phosphate-modified thiodiphenol-containing epoxy resin (P3-ETP) are outlined in Scheme 1. Phosphorus oxychloride was first reacted with bis-thiodiphenol in 1/3 ratio and then reacted with 1/3 molar ratio with Epikote 828 to form the P3-ETP epoxy copolymer by hot melt method. The epoxy equivalent weight (EEW) calculated from ¹H-NMR spectra data for P3-ETP was 714 with the *n* values of 1.50 while the E-1001 possessed the EEW of 580 with *n* of 2.9. The thermal curing procedure of the penta-coordinated P3-ETP and P3-BPA epoxy copolymers with a curative of DMP-30 (5 wt %) was carried out at 120°C for 1 h.

Table I Spectral Characteristics of Phosphate-Modified Epoxy Copolymers

	IR ^a (cm ⁻¹)	¹ H-NMR ^b (ppm)	¹³ C-NMR ^b (ppm)
P3-TDP	3330 (—OH), 1226 (—P=O), 1136 (—P—O—C—)	7.3–6.7 (P-O-phenyl and S-phenyl)	155.4, 135.7, 132.9, 127.1, 116.7, 116.2 (P-O-phenyl and S-phenyl)
P3-ETP ^c	3396 (—OH), 1246 (P=O), 1136 (—P—O—C—), 912 (oxirane)	7.4–6.7 (P-O-phenyl and S-phenyl) 3.3 (oxirane for —O—CH—) 2.9, 2.7 (oxirane for —O—CH ₂) 1.61 [—C(CH ₃) ₂ -phenyl]	155.4, 132.7, 126.8, 115.6, 114.0 (P-O- phenyl, C-phenyl, and S-phenyl) 50.3, 44.8 (oxirane) 31.0, 41.7 [(CH ₃) ₂ -C-phenyl]
P3-BPA	3345 (—OH), 1228 (P=O), 1140 (—P—O—C—)	7.3–6.5 (P-O-phenyl and C- phenyl), 1.6 [—C(CH ₃) ₂ -phenyl]	153.7, 142.7, 128.1, 127.7, 114.9, 114.7 (P-O-phenyl and C-phenyl) 31.0, 41.7 [(CH ₃) ₂ -C-phenyl]
P3-EBPA	3358 (—OH), 1246 (P=O), 1142 (—P—O—C—), 914 (oxirane)	7.2–6.5 (P-O-phenyl and C-phenyl) 3.3 (oxirane for —O—CH—) 2.9, 2.7 (oxirane for —O—CH ₂) 1.6 [—C(CH ₃) ₂ -phenyl]	153.7, 142.7, 130.4, 126.9, 125.6, 114.7, 114.3 (P-O-phenyl and C- phenyl) 49.6, 44.3 (oxirane) 31.0, 41.5 [(CH ₃) ₂ -C-phenyl]

^a Cast on NaCl plate.^b In CDCl₃.

Main spectroscopic data of infrared, ¹H-NMR, and ¹³C-NMR are listed in Table I. The infrared spectra containing the P3-ETP and the starting materials are shown in Figure 1. The infrared absorption peaks of the phosphate moieties of

**Figure 1** The Fourier transform IR (FT-IR) spectra of TDP, P3-TDP, P3-ETP, and DGEBA-E828 resins.

P=O, P—O—C, and the oxirane, for example, are shown in 1246(s), 1098(s), and 914(w) cm⁻¹, respectively. The ¹H-NMR of P3-ETP is shown in Figure 2. The oxirane protons are correlated to the peaks at 2.7 and 2.9 ppm for —O—CH₂—, and at 3.3 ppm for —O—CH— with the corresponding oxirane carbons at 44.8 and 50.3 ppm, respectively, in ¹³C-NMR. Others are listed in Table I.

Curing Kinetics Measurement of the Phosphate-Containing Epoxy Copolymer (P3-ETP)

The dynamic measurement of DSC is one of the methods^{17,18} most often used in the kinetic study of the self-crosslinking behaviors of epoxy resins. The Arrhenius equation is used in accompanying with the rate equation. The temperature dependent rate is shown in eq. (1) and the activation energy is expressed in the Arrhenius eq. (2):

$$r = dx/dt = \beta dx/dT = k(T)f(x) = k(T)(1-x)^n \quad (1)$$

$$k(T) = A \exp(-E_a/RT) \quad (2)$$

where $f(x)$ is the kinetic function; x , fraction conversion; $k(t)$, rate constant; β , heating rate (°C/min); E_a , activation energy (J/mol); A , preexponential factor; R , gas constant; and T , the temperature (K).

A combined eq. (3) from eq. (1) and eq. (2) is shown below:

$$dx/dt = \beta dx/dT = A \exp(-E_a/RT)(1-x)^n \quad (3)$$

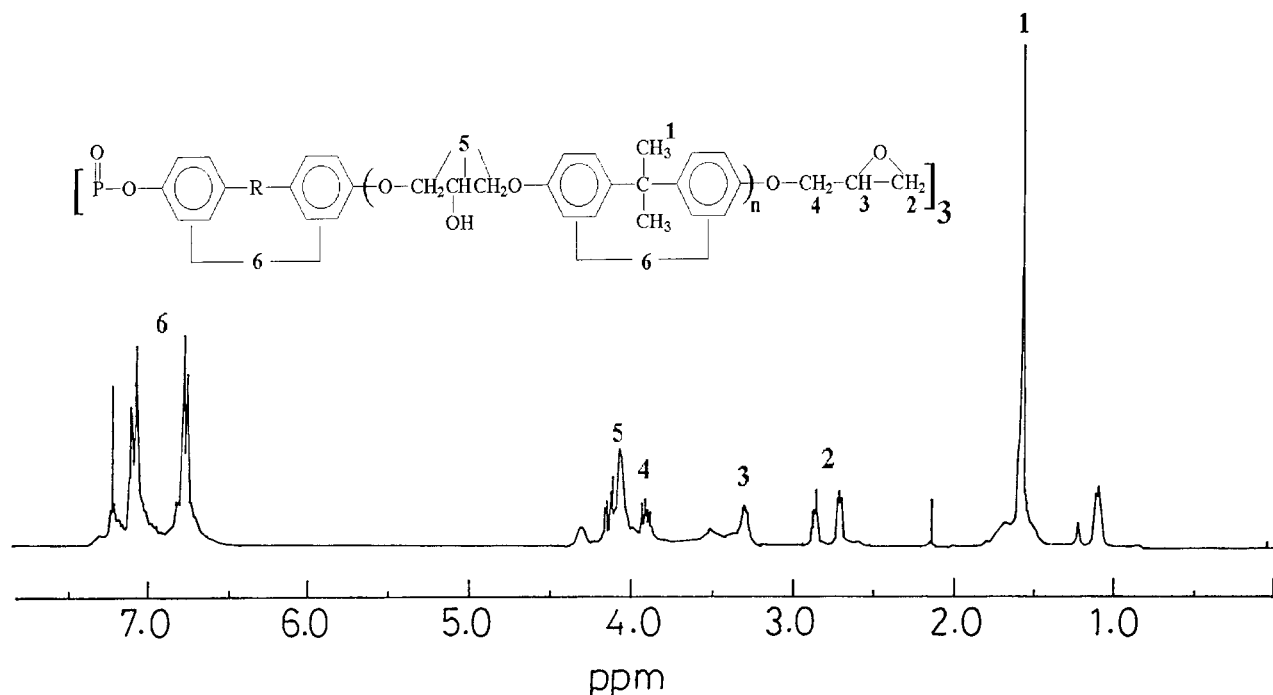


Figure 2 $^1\text{H-NMR}$ of P3-ETP epoxy resin.

A differentiation with time on the eq. (3) was carried out. At the maximum rate, the term $d(dx/dt)/dt$ is zero and gives the eq. (4):

$$\beta E_a/RT_p^2 = An(1-x)_p^{n-1}\exp(-E_a/RT) \quad (4)$$

where T_p is the temperature at the maximum rate in the DSC thermogram.

An epoxy resin known to follow first-order kinetics yields the linear line in the Kissinger treatment.¹⁸ To simplify the measurement, the Kissinger treatment is applied and is used for the kinetic study of the phosphate-containing epoxy copolymer of P3-ETP, since the modification work on the backbone was away from the epoxy segment. The phosphate group, even as the tri-branched junction, is contained in the aromatic segment in backbone. The structure is shown in Scheme 1. The phosphate group is not in the vicinity of the epoxy ring, therefore, the curing behavior of the P3-ETP epoxy copolymer may affect the rate of the self-crosslinking process but should not alter greatly the basic self-crosslinking pattern of the unmodified epoxy sample.

The Kissinger treatment in natural logarithm is shown in eq. (5):

$$-\ln(\beta/T_p^2) = -\ln(AR/E_a) + E_a/RT_p \quad (5)$$

For the polymeric sample with first-order kinetics, a straight line is expected in the plot of $-\ln(\beta/T_p^2)$ to the reciprocal of the temperature ($1/T_p$). The activation energy can then be obtained from the slope of the straight line.

The kinetic measurement of P3-ETP was conducted with the dynamic mode under the self-polymerization condition with a small yet constant amount of the curative to simplify the measurement and to avoid factors that may affect the curing behaviors of the epoxy resin such as the structural alternation as well as the curative properties, among others.^{19,20}

The kinetic study was conducted with the variation of the heating rate. It was varied from 2.5 to 20°C/min under nitrogen atmosphere. Figure 3 shows a typical DSC thermogram for the dynamic measurement. Samples used were the epoxy copolymer with the penta-coordinated phosphate group that contains a 4,4'-thiodiphenolic segment with the glycidyl ether group (oxirane) in the terminal of the tribranches (P3-ETP) with the reference materials of ETP and E-1001 epoxy resins for the comparison. The Kissinger treatment on these samples is shown in Figure 4. A linear relationship indicates that all epoxy samples used in this study showed first-order kinetics with respect to the epoxy resin under constant amount of

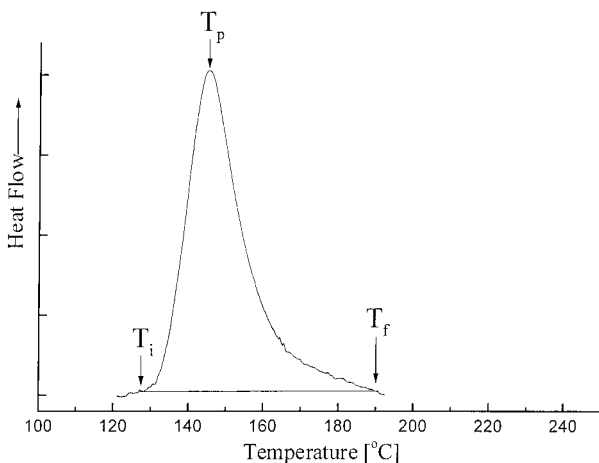


Figure 3 Dynamic DSC thermogram of P3-ETP at a heating rate of 2.5°C/min.

the catalytic curative, DMP-30. The P3-ETP appeared at the lowest end of the reciprocal of the T_p among the phosphate-less ETP and/or E-1001. By the Kissinger treatment, the activation energy E_a , and the collision factor in $\ln A$ are extracted and listed in Table II. These data indicates that the curing rate of the phosphated P3-ETP is the fastest among the resins tested and the order of reactivity is P3-ETP > ETP > E-1001. The rate of phosphate-modified BPA-containing epoxy copolymer, P3-Expoxy resin of bisphenol A (P3-EBPA), was also observed to be faster than ETP and E-1001 as listed in Table II.

A fractional conversion of P3-ETP was then calculated at the various temperatures by using eq. (6):

$$X = \Delta H_T / \Delta H_{\text{total}} \quad (6)$$

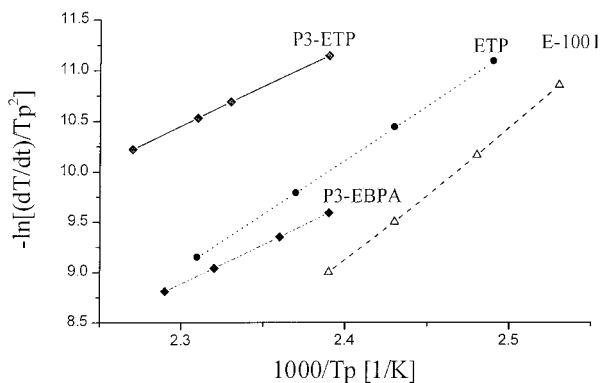


Figure 4 Determination of kinetic order of E-1001, ETP, P3-ETP, and P3-EBPA resins by using the Kissinger treatment.

Table II Kinetic Parameters of Phosphate-Modified Epoxy Copolymers^a

Epoxy	E_a (KJ/mole)	$\ln A$ (min^{-1})
E 828	124.7	31.1
E1001	109.9	25.2
P3-EBPA	66.7	10.7
ETP	89.1	18.0
P3-ETP	61.5	8.5

^a Obtained by using the Kissinger's treatment.

where ΔH_{total} is the total amount of exothermic heat evolved, and ΔH_T is the heat evolved at temperature T .

Figure 5 shows the fractional conversions of the phosphated P3-ETP and the related specimens. Faster curing behavior with a better storage stability is the ideal characteristic for epoxy resins. The fractional conversion curve of P3-ETP appeared at the highest temperature region in Figure 5 among these specimens, indicating that the tribranched phosphate moieties stabilize the epoxy resin. Additional data on the curing properties are listed in Table III. A narrower curing range and shorter curing time of P3-ETP can be observed. For example, P3-ETP cured with the starting temperature $T_i = 130^\circ\text{C}$, peaked at $T_p = 145^\circ\text{C}$, and completed at $T_f = 188^\circ\text{C}$. E-1001, which started to cure at a lower temperature of $T_i = 92^\circ\text{C}$, peaked at $T_p = 122^\circ\text{C}$, and completed at a higher temperature of $T_f = 193^\circ\text{C}$, compared to P3-ETP under the same curing condition. The curing range of 58°C for P3-ETP is much narrower than the curing range of 101°C for E-1001.

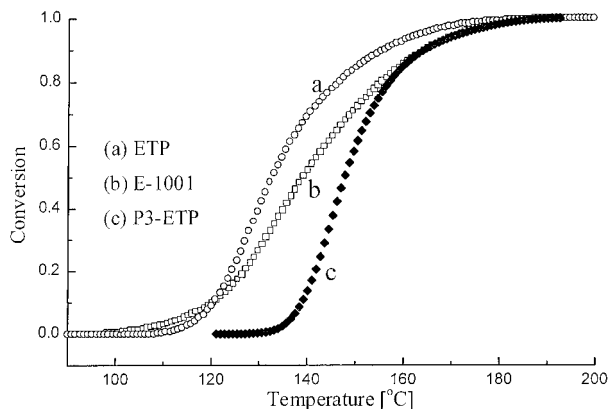


Figure 5 Fractional conversion as a function of temperature for a heating rate of 2.5°C/min. (a) ETP, (b) E-1001, and (c) P3-ETP.

Table III Curing Characteristics of Phosphate-Modified Epoxy Copolymers^a

	T_i (°C)	T_p (°C)	T_f (°C)	Curing Range (°C)	Curing Time (min)
E828	51	92	156	105	42.0
E1001	92	122	193	101	40.4
P3-EBPA	100	146	165	65	26.0
ETP	109	129	169	60	24.0
P3-ETP	130	145	188	58	23.2

^a From DSC measurements at heating rate of 2.5°C/min.

Consequently P3-ETP possesses a shorter curing time in 23.2 min to E-1001 in 40.4 min. It is therefore concluded that the phosphated epoxy specimen of P3-ETP possesses improved curing properties with a shorter curing temperature range and a faster curing time, as indicated in Table III. The higher initial curing temperature of the P3-ETP ($T_i = 130^\circ\text{C}$) indicates the better shelf stability for the storage at the ambient condition than the E-1001 ($T_i = 90^\circ\text{C}$). The additional thermal characteristics, especially the thermal stability related to the flame retardancy, were evaluated with the TGA as follows.

Total Analysis of Thermal Degradative Behaviors of P3-ETP

TGA Measurement

Incorporation of the aromatically tribranched phosphate moieties in the epoxy backbone may provide an additional property in flame retardancy, which is often expressed by the LOI

value. Figure 6 shows the TGA diagram of P3-ETP, P3-EBPA, ETP, and E-1001 in air (solid symbol) and under nitrogen atmosphere (open symbol). The char yield under N_2 atmosphere at 850°C was 33.0% for P3-ETP, 24.8% for P3-EBPA, and 9.0% for E-1001, respectively, in the TGA measurement at a heating rate of $20^\circ\text{C}/\text{min}$. This high char yield of the phosphated epoxy specimen of P3-ETP indicates better thermal stability for the phosphate-containing epoxy specimens (33.0% for P3-ETP and 24.8% for P3-EBPA) compared to the unmodified diglycidyl ether of bisphenol A (DGEBA) epoxy resin (9.0% for E-1001). The difference in stability may be related to the thiodiphenol linkage. The same linkage with excellent thermal stability is known for polyphenylsulfide (PPS).^{21,22}

One interesting phenomenon as observed in Figure 6 for the phosphate-containing epoxy specimens of P3-ETP and P3-EBPA is the showing of the better thermal stability at $500\text{--}600^\circ\text{C}$ in air than under nitrogen atmosphere. This phenome-

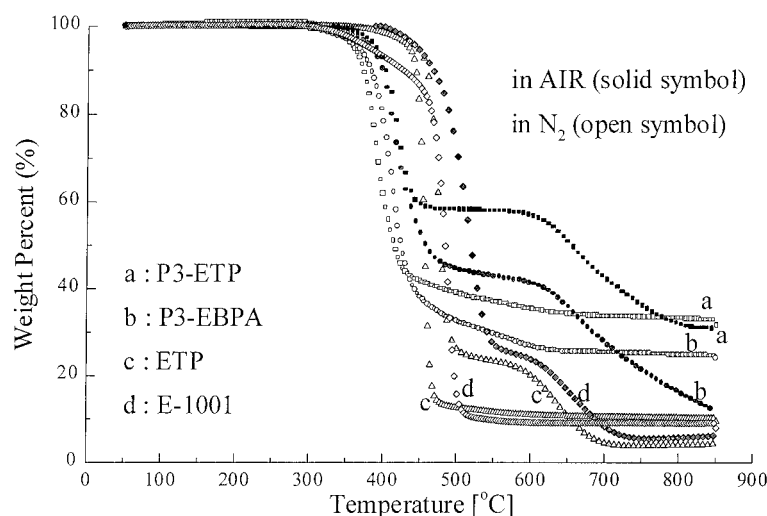


Figure 6 TGA thermograms of various epoxy specimens under air and nitrogen atmospheres.

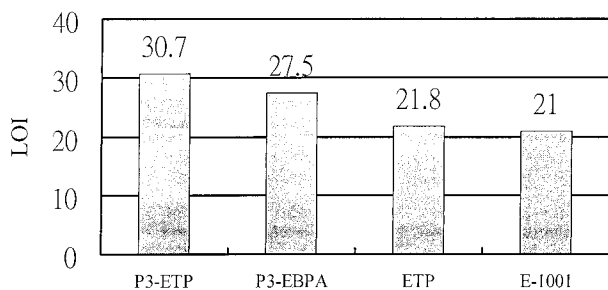


Figure 7 LOI values of the phosphate-modified epoxy specimens with references.

non, with the observation of a slower weight loss curve occurring in air compared to N_2 near $400^\circ C$, may indicate that the organophosphate is converted into inorganic phosphate^{23,24} in this temperature region. The thermal transformation of organophosphate into the inorganic phosphate is faster in air than under a nitrogen atmosphere. Therefore, these phosphate-containing P3-ETP and -EBPA provided a better thermal stability at $500\text{--}600^\circ C$ under atmospheric conditions. It was indicated that the inorganic phosphate prevents further degradation as it may coat on the surface of specimens.^{23,24} At a higher temperature above $600^\circ C$ under air, a further decomposition took place and reduced the char yield from 33.0% (N_2) to 30.6% (air) for P3-ETP. A similar reduction for P3-EBPA specimen was seen in Figure 6.

The Calculation of the LOI Value

The LOI values for phosphate-modified epoxy specimens of P3-ETP and P3-EBPA can be calculated from the char yield of the TGA measurement under the N_2 atmosphere. LOI value represents the minimum needed oxygen fraction in a nitrogen–oxygen (air) mixture for the maintenance of the combustion. The correlation of LOI to the char yield (CR) is expressed in eq. (7)¹⁶:

$$\text{LOI}(\%) = 17.5 + 0.4(\text{CR}) \quad (7)$$

where CR is the char yield in weight percent at $850^\circ C$ under the nitrogen atmosphere.

The calculated LOI values for P3-ETP and related compounds are compared in Figure 7. P3-ETP with 30.7% surpasses the minimum LOI value of 26%. This minimum LOI value has been used to indicate the minimum requirement for the materials to be regarded as a nonflammable material. Therefore, P3-ETP and the P3-EBPA

with LOI value of 27.5% both meet the requirement as a nonflammable material.

The LOI values of unmodified ETP and E-1001 are 21.8 and 21.0%, respectively, and failed to meet the minimum requirement to be regarded as nonflammable for the material.

The Analysis of the Char Residue

The nature of the char yield was subjected to further analysis. Figure 8 shows the infrared spectrum of the char yield. No defined organic functional groups were detected, indicating that the residue could be composed of carbon (judged from the appearance) and possibly with inorganic materials. The examination on char residues of P3-ETP and P3-EBPA was carried out by SEM/EDX instrument. Figure 9 shows the EDX electrogram of the char residue of the P3-ETP. The absorption peaks were related to the P and S elements. The P element shows an EDX peak at 2.013 KeV and S element at 2.307 KeV, respectively. Based on this analysis, the char yield may contain phosphate and sulfate salts as the P and S elements are present in the P3-ETP. This analysis supports the findings indicated in the literature^{23,24} that the formation of the phosphate salt that coated on the surface of the plastics is the prerequisite for the prevention of thermal degradation.

DP-GC/MS Measurement of the TDVs

TDVs emitted from the phosphate-modified thiodiphenol-containing P3-ETP were subjected to DP-GC/MS analysis at $900^\circ C$ after instant pyrolysis. The TDVs were then injected on to a GC

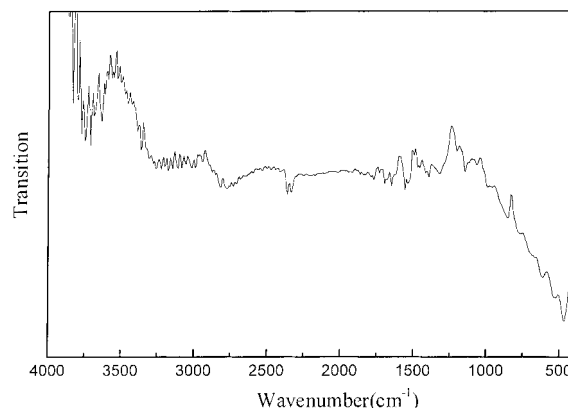


Figure 8 FTIR spectrum of char residue of P3-ETP from TGA experiment under the nitrogen atmosphere.

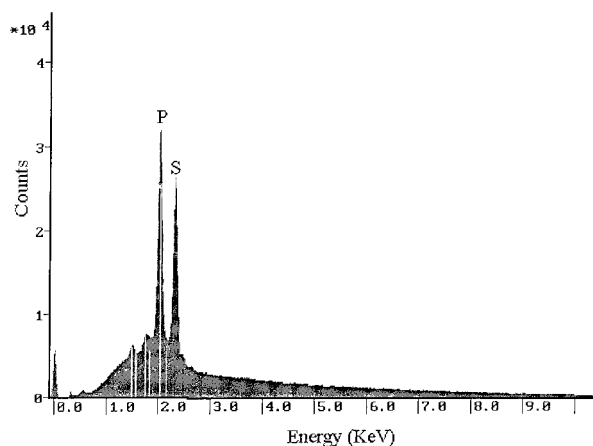


Figure 9 EDX electrogram of char residue of P3-ETP copolymer from TGA experiment under nitrogen atmosphere.

column and then subjected to mass analysis. The total ion current from the DP step was separated into single ion current (SIC) in the GC step and analyzed by the mass detector. The SIC peaks of the phosphate-containing sample (P3-ETP) can be seen in Figure 10(a) while the SIC peaks from the phosphate-less sample of the ETP is shown in Figure 10(b). A similar SIC mass distribution was observed in both specimens, indicating that the basic thermal degradation was not altered by the phosphate modification on the epoxy backbone, if the instant thermal degradation was carried out at 900°C. Some SIC structures elucidated from

the individual mass fragmentations are listed in Table IV. However, the delaying appearances of SIC ions, particularly on the retention times of the SIC ions of $m/z = 91$, 94, and 121 from phosphate-containing P3-ETP, were observed over the unmodified ETP sample.

To simplify the degradative products, a four-staged procedure was then conducted. The emitted TDVs from each thermal degradative stage were subjected to the DP-GC/MS analysis. The selection of the four stages was arbitrary but took account of the TGA data (Figure 6) and the elaborated experiments on the DP-GC/MS measurement. The heating at stage I was from ambient to 350°C, stage II was 350–400°C, stage III was 400–450°C, and stage IV was from 450–500°C in the analysis.

These SIC spectra are shown in Figure 11, where (a) represents the main portion of the GC/MS spectra of ETP and (b) for the P3-ETP under the same condition. For ETP, the phosphate-less sample, the observed SIC ions appeared consistently with the same pattern in GC/MS spectra throughout the entire four stages while the P3-ETP showed a different pattern of degradation in this four-staged pyrolysis. The main TDVs from ETP sample was the SIC with $m/z = 170$, which appeared in 11.45 min throughout all four stages. The structural elucidation of this SIC as shown in Figure 12 was based on its fragmentation data of $m/z = 170$, shown in Figure 13. For ETP, the thermal degradation started

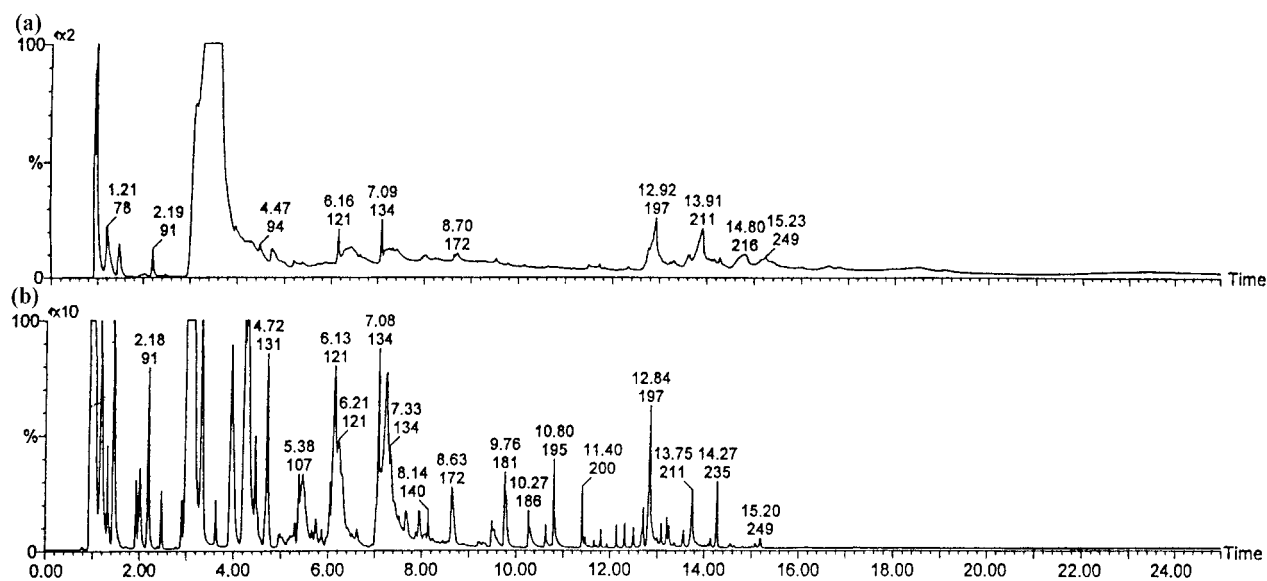
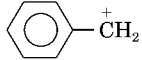
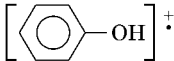
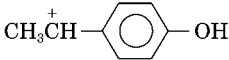
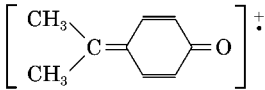

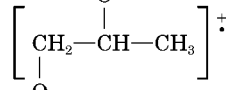
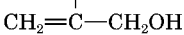
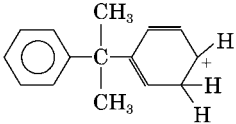
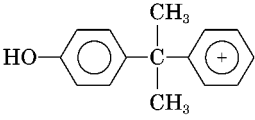
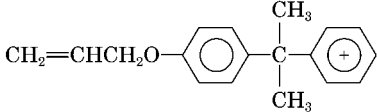


Figure 10 DP-GC/MS spectra of the TICs emitted at 900°C (a) P3-ETP and (b) ETP.

Table IV DP-GC/MS Measurements on P3-ETP and ETP Specimens

m/z	Retention Time (min)		SIC Ion with Suggested Structure ^a
	ETP	P3-ETP	
91	1.44	1.46	
94	3.13	3.92	
121	6.13	6.36	
134	7.08	7.09	 
172	8.63	8.70	 
197	12.84	12.92	
211	13.75	13.91	
249	15.20	15.23	

^a Based on its mass fragmentation.

at the crosslinked glycidyl ether segment as well as at the aromatic moiety, which was then transformed to the phenol.

On the other hand, the phosphate-containing epoxy specimen, the degradation pattern was different from that of ETP, since no thermal degradative volatile with $m/z = 170$ was found. Probably thermal degradation of P3-ETP was affected by the enlarged matrix by the tribranched phos-

phate junction. The enlarged space among the branched chain of P3-ETP or P3-EBPA degrade in thermal degradation process from each chain with the enlarged space among them. An oversimplified fragmentation is shown in Figure 14 with the data from mass fragmentations of the key SIC ions of $m/z = 213$ and 134, shown collectively in Figure 15. At stages I and II, the larger SIC ions of 213–94 were emitted as the main TDVs, while

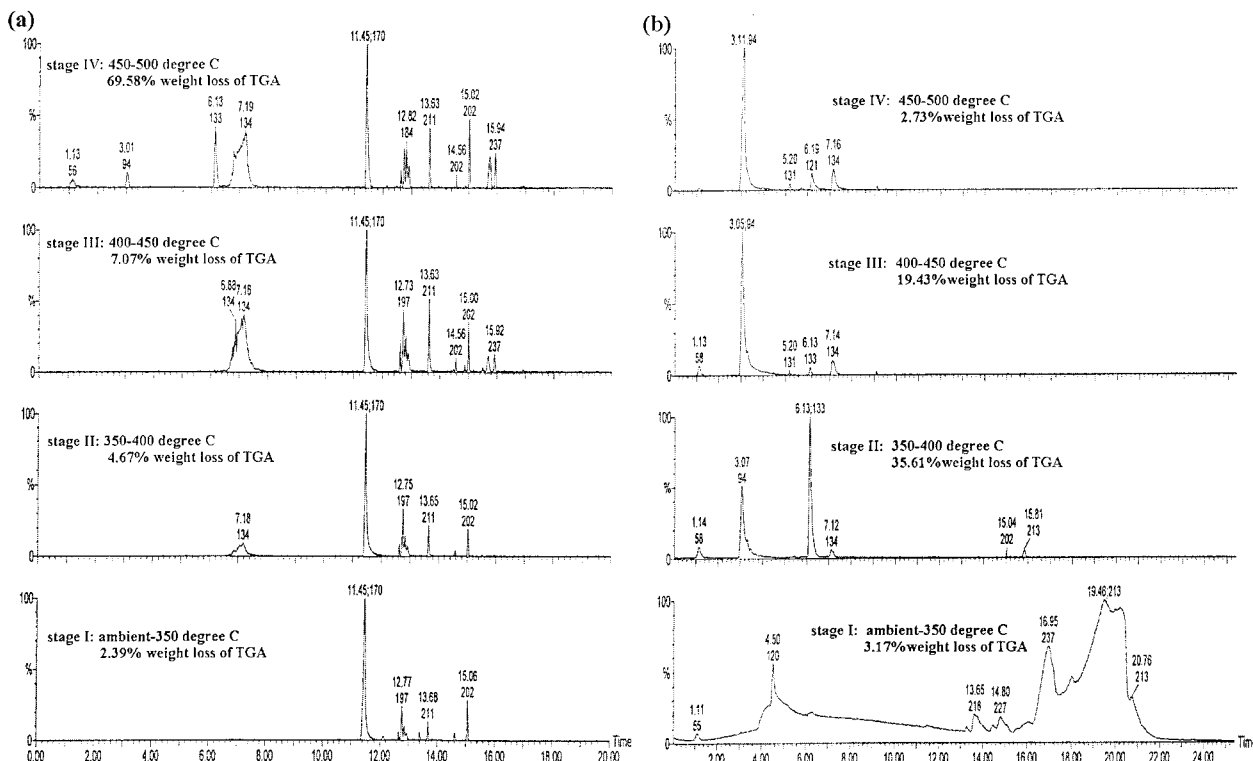


Figure 11 The DP-GC/MS spectra for SICs at stage I: ambient–350°C; II: 350–400°C; III: 400–450°C; IV: 450–500°C. (a) ETP and (b) P3-ETP.

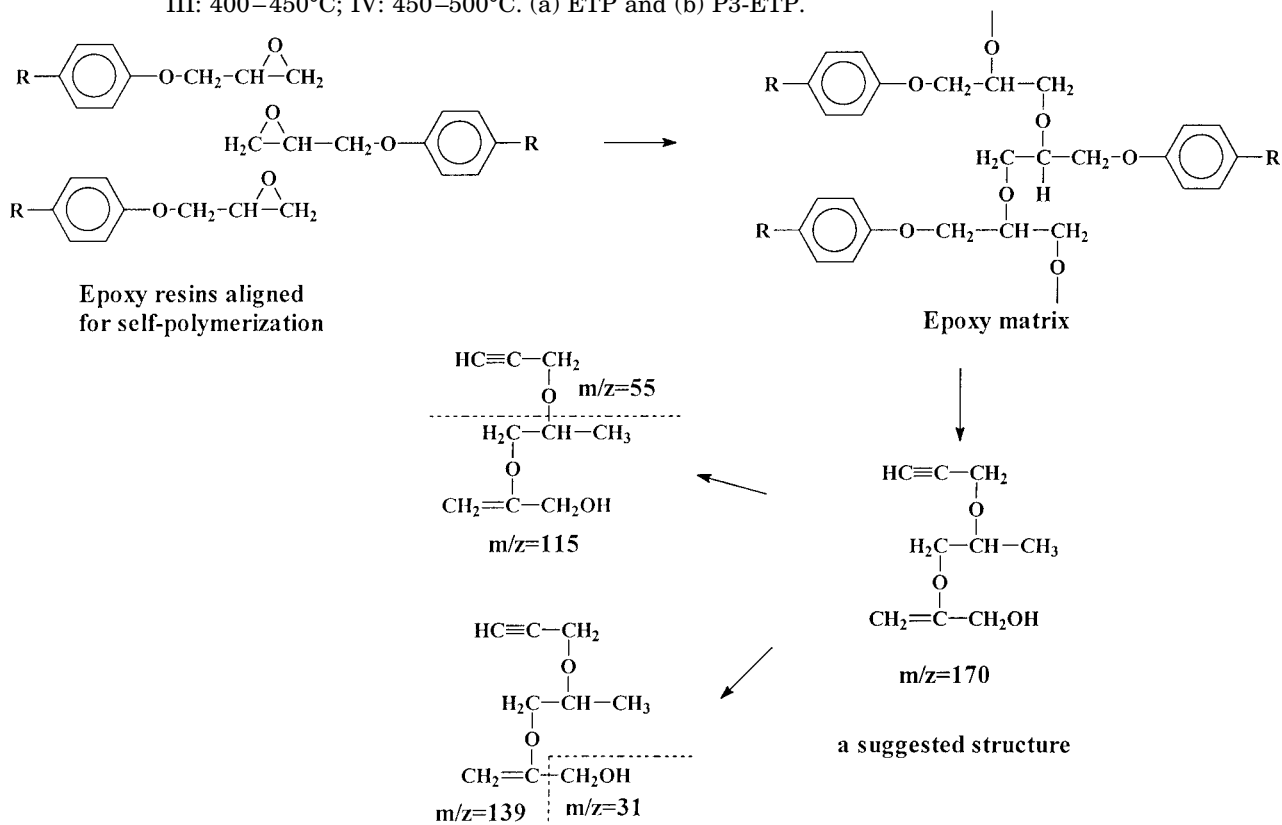


Figure 12 The proposed formation and the mass fragmentation of the key TDV with $m/z = 170$.

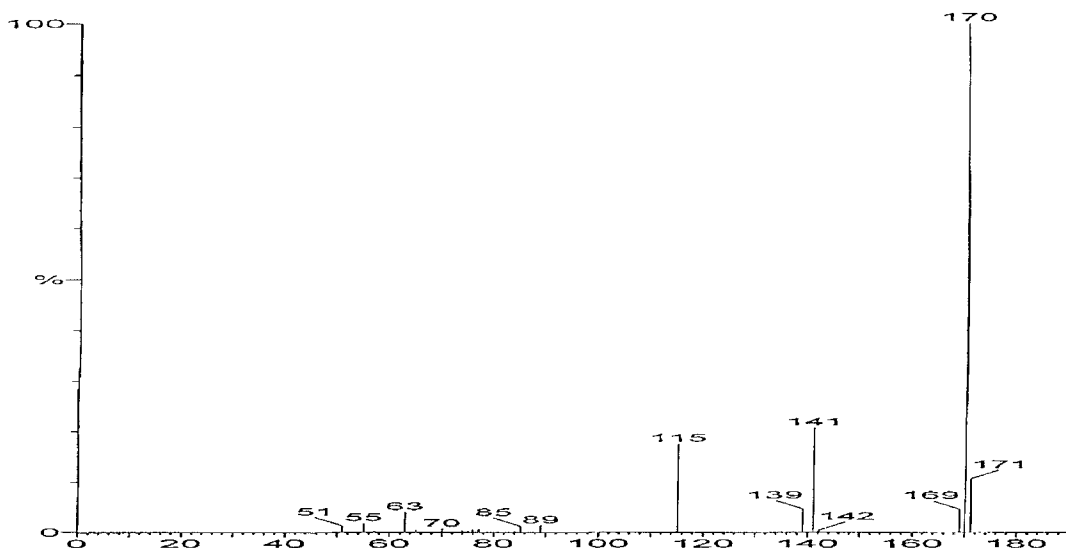


Figure 13 Mass fragmentation of a key SIC, $m/z = 170$.

at higher temperatures in stages III and IV the emission was limited to the aromatic SIC ions of $m/z = 134$ and 94 , which could be formed

through secondary degradations of the larger SIC ions such as $m/z = 305$ to 213 . The SIC with $m/z = 94$, the phenol, could also be formed from the

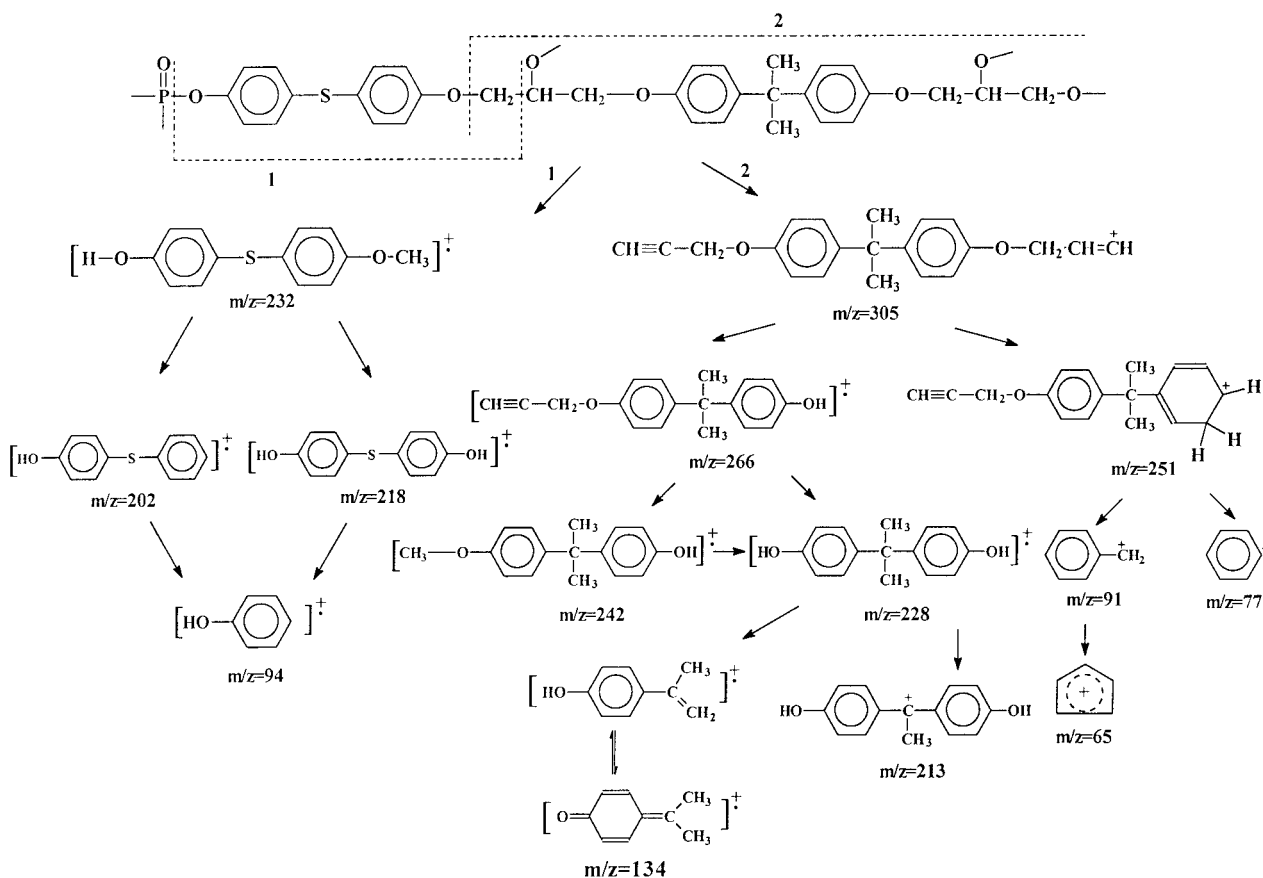


Figure 14 An oversimplified mass fragmentations of P3-ETP epoxy matrix.

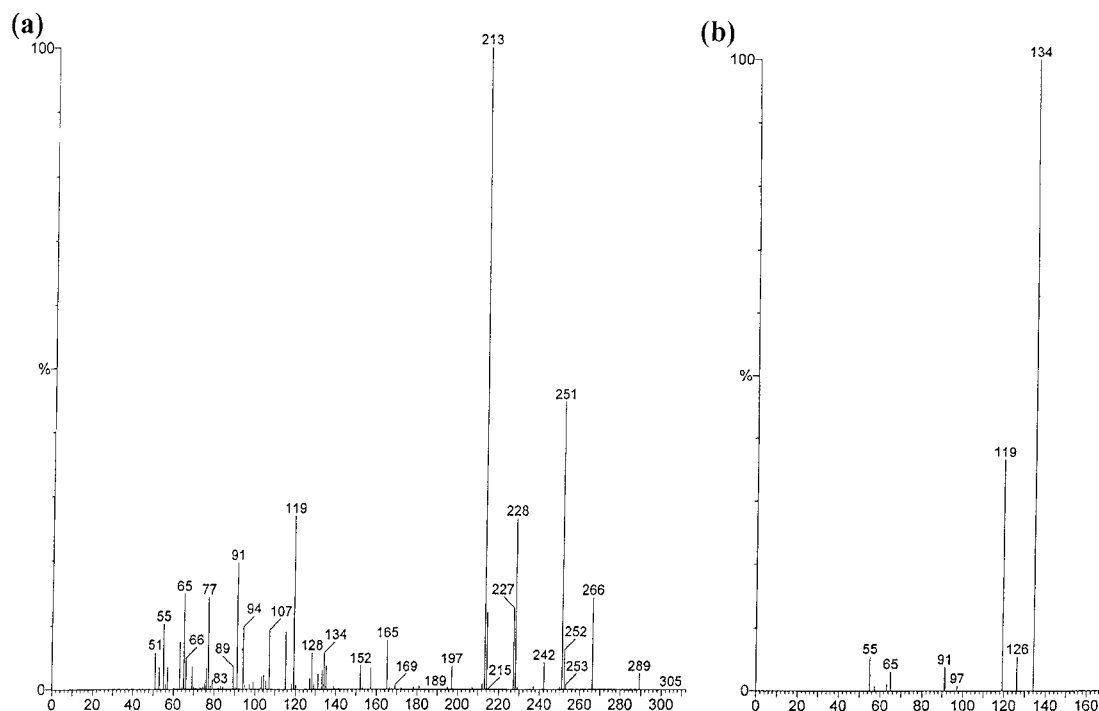


Figure 15 Mass fragmentations of SICs (a) $m/z = 213$ and (b) $m/z = 134$.

phosphate moieties of P3-ETP. The $m/z = 94$ appeared with a much broadened peak at the high temperature at 900°C as earlier shown in Figure 10. An explanation for this broadened SIC peak may be due to the blocking effect of phosphate moiety after it was transformed into an inorganic salt as it may coat the surface of the specimen. The slowing down of the thermal degradation of the epoxy specimen by P3-ETP may therefore be seen from delayed emission of the thermal degradative volatiles in these measurements.

The DP-GC/MS analysis based on the emission of the TDVs may show the thermal degradative pattern of the epoxy matrix. As expected, the aliphatic segment in the epoxy matrix was first to degrade thermally as illustrated with the consistent appearance of SIC $m/z = 170$ in stages I–IV. On the other hand, the phosphate-containing P3-ETP specimen started with the TIC formations with mass units ranged from 213 to 237 at stage I from ambient temperature to 350°C in Figure 11(b). At 400 – 500°C , aromatic TDVs began to appear and the main peak was $m/z = 94$. These data indicated that at stage I, at the temperature from the ambient to 350°C , the epoxy specimen was subjected to the same degradative pattern as shown in the phosphate-less ETP epoxy specimen in Figure 11(a). However, the SIC of 213 and

related ions diminished as the temperature increased from stages III to IV or the temperature from 400 to 500°C . The suppression of the formation of SIC of 170 was clearly indicated by the phosphate-containing P3-ETP in Figure 11(b) at temperatures above 400°C . At the same time, the formation of the phenol with $m/z = 94$ was increased as the organophosphate moieties were decomposed to form the expected inorganic phosphate salt for the blocking effect of the thermal degradation of P3-ETP. This result also provides an explanation as to the high char yield of the P3-ETP in the TGA analysis.

CONCLUSION

Thermal kinetics of the curing process of P3-ETP was found to follow first-order curing pattern that obeys the Kissinger equation similar to the unmodified DGEBA epoxy resins. P3-ETP epoxy resin possesses improved curing properties of a narrower curing temperature range among others. A higher initial curing temperature may indicate the better storage stability at the ambient temperature. The low activation energy for P3-ETP of phosphated epoxy resin as indicated by the faster curing behavior may associate with the

better mobility of the oxirane group in matrix. The penta-coordinated phosphate moiety in the epoxy backbone is highly polarized group with $[O=P(O)_3-]$ and may act as a polar medium thus facilitates the mobility of the epoxy group for the self-polymerization. Thermal stability of this modified epoxy copolymer, P3-ETP, shows a high LOI value of 30.7, indicating the improvement on the nonflammability by the phosphate-containing epoxy resin. The DP-GC/MS analysis on the thermal degradative volatiles in terms of four temperature ranges from ambient to 500°C indicates that epoxy matrix started to degrade from the aliphatic segment around 350°C and followed by the aromatic segmental degradation above 400°C. The phosphate moiety may shield the degradation of the epoxy matrix only after its thermal transformation from organophosphate to inorganic phosphate above 400–500°C. The effect of the phosphate moieties in the epoxy matrix was observed with the delaying appearance of the TIC at 900°C and confirmed by the staged-degradation study with the analysis of the SIC spectra from ambient to 500°C in four stages.

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