

Thermal Degradation Behavior of Epoxy Resin Blended with Propyl Ester Phosphazene

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ABSTRACT: The study was focused on the thermal degradation behavior of epoxy resins (EP) blended with propyl ester phosphazene (FR). The analysis studied the evolved gas and the residual char yield using different techniques. The results showed that pure epoxy resin and their blends were all a one-stage thermal degradation reaction. The major degradation temperature of blends was lower than the temperature of pure epoxy resin, but the residual char yield of epoxy blends at 550°C was higher than that of pure epoxy resin. FR could accelerate the production of small molecules such as acetone, phenol, and isopropyl phenol during thermal degradation process. Honeycomb structure compounds were also formed in the residual char of epoxy and its blends. Additionally, elemental analysis of the residual char yield showed that phosphorus was a residual element, and other elements mostly diffused to the evolved gas. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 81: 1161–1174, 2001

Key words: blends; epoxy resin; propyl ester phosphazene; pyrolysis mechanism; thermal degradation

INTRODUCTION

Due to the excellent mechanical properties and adhesion, epoxy resins are widely used in aerospace and other fields. Although they have excellent chemical and mechanical properties, they are not stable at high temperatures. Many studies about thermal degradation of epoxy resin had been reported. For example, Grassie et al.¹ had used the subambient thermal volatilization analysis procedure (SATVA) to examine the products

evolved during the thermal degradation of epoxy resin, and proposed the thermal degradation mechanism from the viewpoint of the bond energy. They suggested that because oxygen and nitrogen atoms have greater negative inductive effect than other atoms, the scission of epoxy resin would take place at O—CH₂ and C—N bonds to form phenol, amine, and other small related molecules. Bellenger et al.² had studied the thermal degradation behavior of diglycidyl ether bisphenol A (DGEBA) and tetraglycidyl methylene dianiline (TGMDA) epoxy prepolymer cured with different amines such as diethylene triamine (DETA), *iso*-phorone diamine (IPD), diamino diphenyl sulphone (DDS), and diamino diphenyl ether (DDE) under the oxidative and non-oxidative conditions. The thermal degradation mechanism was influenced by the curing agents, amine concentration, and the nitrogen atom nu-

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cleophilicity. Recently, many literatures³⁻⁵ have reported that phosphorus-containing compounds can be used as additives to improve the thermal stability of many polymers besides epoxy resins. For example, Denq et al.⁵ reported propyl ester phosphazene, used as a flame retardant with high phosphorous and nitrogen content, would react with PMMA to form an anhydride structure that could increase the major thermal degradation temperature. Other reports^{6,7} have point out that phosphorus-containing compounds would form phosphorus-like acid structure during the thermal degradation. The function of phosphorus-like acid was stated as follows:

1. Cyclic structures⁶ were formed by dehydration, and by further degradation they could break into a variety of small molecules.
2. Free radicals^{6,7} in the gas phase were captured by the phosphorus-like acid. Both the volatile and combustible gases on the surface were insulated by the formed carbonaceous char to stop the further thermal degradation.
3. Epoxy resins⁷ blended with organophosphonic compounds containing phosphorus, chloride, or nitrogen would produce nonvolatile residuals during the thermal degradation. These nonvolatile residuals could form thermostable structures with aromatic C—Cl and P=N bonds.

In our previous study,⁸ the curing kinetics and physical properties of epoxy resins (DGEBA/DETA) were deeply influenced by the FR content. The detailed studies on the thermal degradation of epoxy resins blended with FR have been not yet reported, and therefore, we investigated it using different analytical techniques in this study.

Table I Composition and Phosphorus Content of Blended Samples

Code	Weight Ratio (DGEBA/DETA/FR)	P (wt %)	
		^a	^b
Ep0f	89.37 : 10.63 : 0	0.00	<0.01
Ep1f	82.04 : 9.75 : 8.21	1.91	1.86
Ep2f	75.82 : 9.02 : 15.16	3.50	3.47
FR	0 : 0 : 100	21.0	21.0

^a Phosphorus content from composition calculation.

^b Phosphorus content by the colorimeter.¹⁰

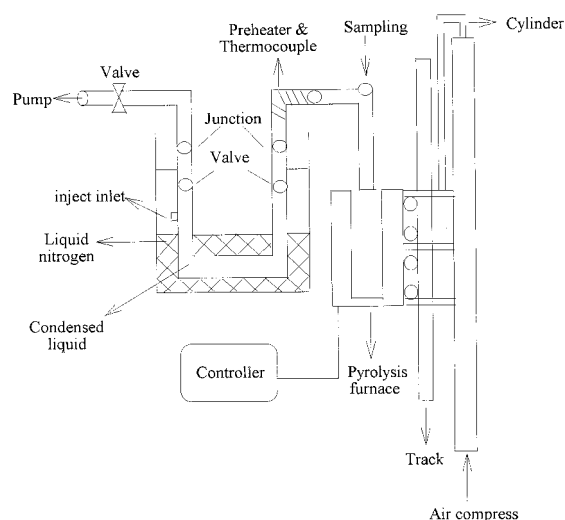
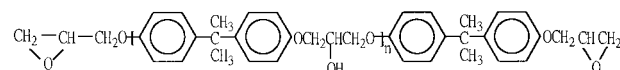


Figure 1 The scheme of apparatus used to degrade and collect volatile products.

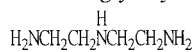
EXPERIMENTAL

Materials

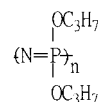
The epoxy prepolymer used in this study was diglycidyl ether bisphenol A (DGEBA) (DER 331, from Dow Chemical Company) with a molecular mass of 380 g/mol (epoxide equivalent weight⁹ of 190 g/Eq). A stoichiometric amount of diethylenetriamine (DETA, from Janssen Chimica Company) with a molecular mass of 103.15 g/mol (amine equivalent weight of 20.63 g/Eq) was used as a curing agent. Propyl ester phosphazene (FR) was supplied by Chung Shan Institute of Science and Technology. The chemical structure of these materials are shown below:



Diglycidyl ether of bisphenol A (DGEBA)



Diethylenetriamine (DETA)



Propyl ester phosphazene (FR)

The formulations of epoxy blended with various amount of FR were shown in Table I and were referred as Ep0f, Ep1f, and Ep2f, respectively. The cure cycle of samples was: precure temperature of 75°C for 2 h and postcure temperature of 95°C for 1 h under atmosphere.

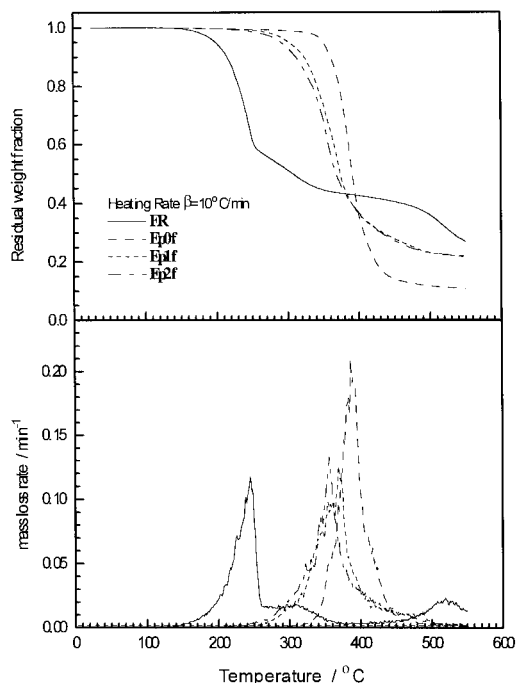


Figure 2 TG-DTG thermograms of FR and epoxy blends at a heating rate of 10°C/min under nitrogen atmosphere.

METHODS

Thermal Degradation

The thermal degradation was examined by a Perkin-Elmer TGA-7 thermogravimetric analysis (TGA) at the heating rate of 10°C/min under a nitrogen atmosphere with a flow rate of 40 mL/min.

Analysis of Evolved Gas

Method 1: TGA/FTIR

The gas products of degraded epoxy blends were investigated using a SEIKO SSC 5000 thermo-

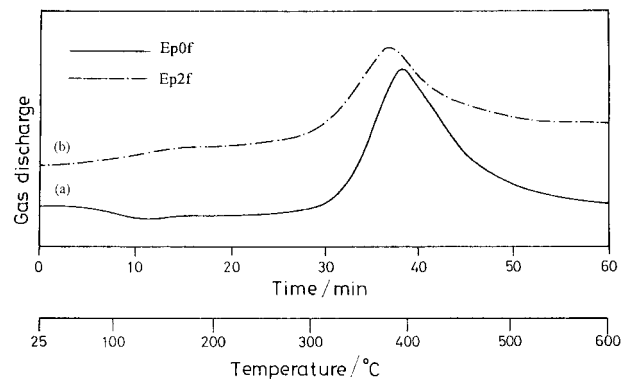


Figure 3 The gas discharge with time (temperature) during thermal degradation for (a) Ep0f and (b) Ep2f at a heating rate of 10°C/min.

gravimetric analysis coupled with a BIO-RAD FTS-40 Fourier transform infrared spectrometer (TGA-FTIR). Samples were heated at a heating rate of 10°C/min under a nitrogen atmosphere with a flow rate of 40 mL/min. The FTIR spectra were identified by visual analysis and by searching the spectral data bases.

Method 2: Pyrolysis/GC/MS

The gas products during the degradation of epoxy blends, about 600 μg , at various temperatures were investigated using a pyrolyzer (Gas pyroprobe CDS-2000) coupled with a gas chromatography (Hewlett-Packard 5890 series II) equipped with a thermal conductivity detector (TCD), and a capillary column (Hewlett-Packard HP-5, 30 m long \times 0.25 mm i.d. coated with the crosslinking packing of 5% diphenyl and 95% diphenyl polysiloxane). The heating rate was set to 200°C/ms in these experiments. The GC conditions were designed to separate the pyrolysis products based on their boiling points and was operated under the following operating parameters: the column

Table II Characteristics of Thermal Degradation of Various Blends at Heating Rate of 10°C/min

Blends	$T_{5\%}/^{\circ}\text{C}$	% Residual at 550°C	Temperature Range/ $^{\circ}\text{C}$		
			Stage 1	Stage 2	Stage 3
FR	224.98	37.47	140–268	271–340	340–550
Ep0f	351	14.6	—	317–550 ^a	—
Ep1f	302	23.9	—	250–550 ^a	—
Ep2f	291	24.3	—	231–550 ^a	—

^a The major degradation temperature of epoxy or its blends is located in the second stage degradation of FR.

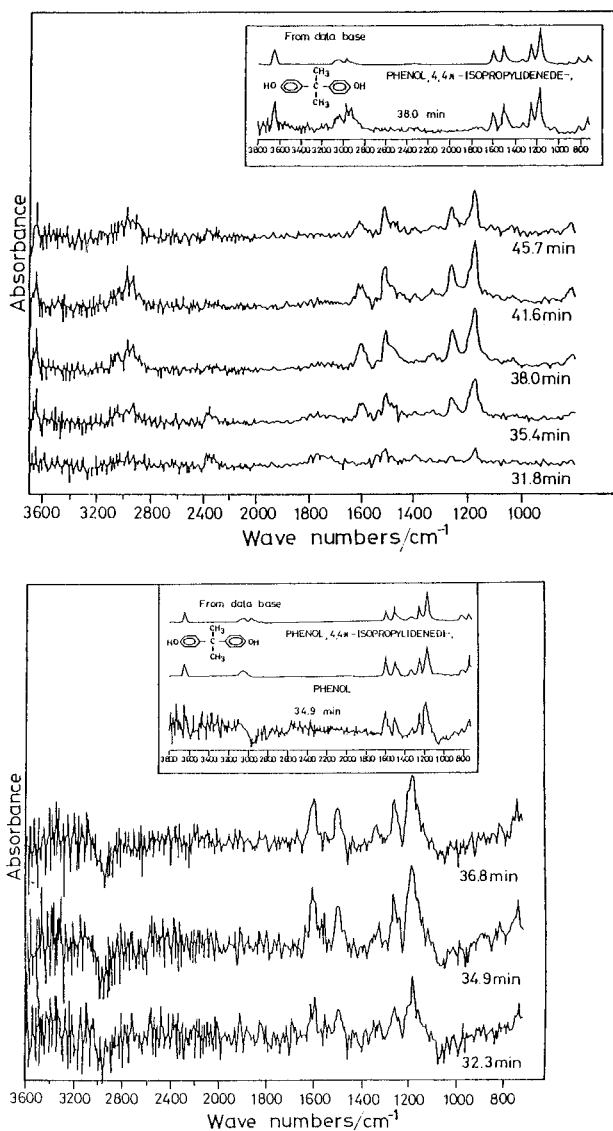


Figure 4 FTIR spectra of gas phase evolved at various thermal degradation time for (a) Ep0f and (b) Ep2f.

injection temperature was set to 220°C; the column operated isothermally at 40°C for 2 min and then heated to 220°C at the heating rate of 10°C/min; the carrier gas was helium with a flow rate of 50 mL/min. The spectra of the evolved gases were identified using a mass detector (Hewlett-Packard 5971) with the scanning range of m/e from 30 to 400 operated at 70 eV, and compared with the spectral databases and literature.^{1,11,12}

Method 3: Separation/GC/MS

Thermal degradation of epoxy resins was carried out in the apparatus shown in Figure 1. The powdered sample, of about 8 g mass, was put in the

T-shape tube and heated to certain temperature with the heating rate of 10°C/min under vacuum. The gases, evolved during degradation, were divided into three types: (i) products with boiling point lower than liquid nitrogen temperature, which remained in the gas state under liquid

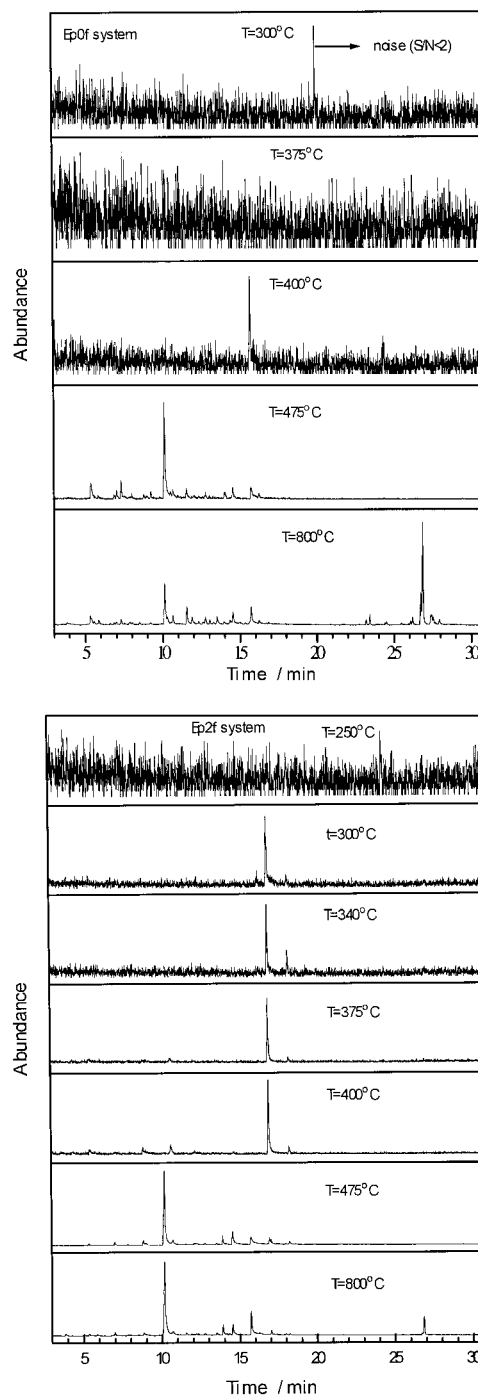


Figure 5 Various pyrolysis GC profiles at different temperature for (a) Ep0f and (b) Ep2f.

Table III Volatile Products of Thermal Degradation of Epoxy Resin and Its Blends Identified by Mass Spectra and Literature^{1,11,12}

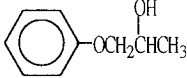
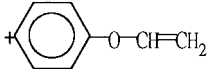
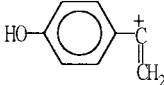
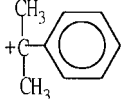
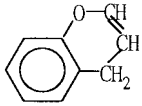
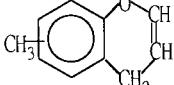
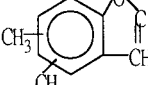
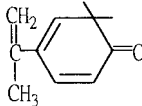
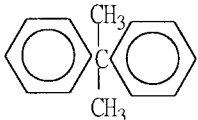
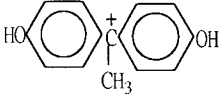
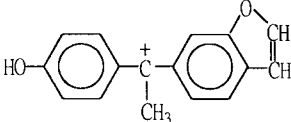
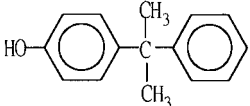
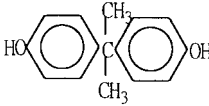
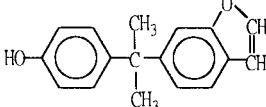
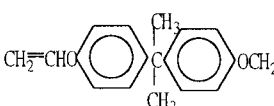
Evolved Time (min)	<i>m/e</i> Value	Compound	Identified Method ^b
5.391	79	unidentified	—
6.887	93	pyridine	L
7.025	105	unidentified	—
8.851	108	(<i>o, m, p</i>)-cresol or methoxy benzene	L
9	152		P
10.115	108	(<i>o, m, p</i>)-cresol or methoxy benzene	L
10.125	108	(<i>o, m, p</i>)-cresol or methoxy benzene	L
10.184	94	Phenol	L
10.632	119	  	P
10.646	122	(<i>o, m, p</i>)-ethyl phenol or ethoxy benzene or dimethyl phenol ^a	L
11.536	122	(<i>o, m, p</i>)-ethyl phenol or ethoxy benzene or dimethyl phenol ^a	L
11.876	108	(<i>o, m, p</i>)-cresol or methoxy benzene	L
12.058	136	(<i>o, m, p</i>)-isopropyl phenol	L
12.727	132		P
13.015	136	(<i>o, m, p</i>)-isopropyl phenol	L
13.054	146	 OR 	P
14.553	136	(<i>o, m, p</i>)-isopropyl phenol	L
15.745	134		L
16.922	183	unidentified	—
23.178	196		L
23.414	213		P

Table III *Continued*

Evolved Time (min)	<i>m/e</i> Value	Compound	Identified Method ^b
26.056	237		P
26.727	212		P
26.858	228		L
27.527	252		P
27.932	270		P

^a Represent the existence of various substituted position of benzene ring.

^b L: library searching; P: proposed by literature.

nitrogen quench; (ii) products with boiling point between liquid nitrogen temperature and room temperature, which was the gas state at room temperature and the liquid state under liquid nitrogen quench; and (iii) products with boiling point higher than room temperature, which was the liquid state at room temperature and under liquid nitrogen quench.

The products type (i) and (ii) were analyzed using a gas chromatograph (GC) (Shimadzu GC-14A) equipped with a flame ionization detector (FID) and a packing column (Shimadzu, 15 m long coated with Al₂O₃/KCl), under the following operating parameters: the column injection temperature was 200°C; the column operated isothermally at 30°C for 10 min and then heated to 180°C at the heating rate of 7.5°C/min; the carrier gas was nitrogen with a flow pressure of 2 kg/cm². The spectra of product type (i) and (ii) were compared with ref. 13.

The products type (iii) were used the similar pyrolysis/GC/MS equipment and the condition to separate and to identify them, but the equipment was without a pyrolyzer.

Analysis of Residual Char Yield

The residual char yields after TGA analysis were pressed into pellets with potassium bromide and studied using Fourier transform infrared spectrometer. Additionally, elemental analysis of the residual char yield was also done using elemental analyzer (F002 Heraeus CHN-O Rapid Elemental Analyzer) to determine carbon, hydrogen, oxygen, and nitrogen content.

RESULTS AND DISCUSSION

Thermal Degradation of Epoxy Blends

In Figure 2 thermogravimetric (TG) curves (residual weight fraction vs. temperature) and the corresponding thermogravimetric DTG curves (mass loss rate vs. temperature) for FR and epoxy blends were shown. In Table II some characteristics of these curves were listed. In our previous study,³ the thermal degradation of FR could be divided into three stages. The evolved gas in the first and second stage was predominantly pro-

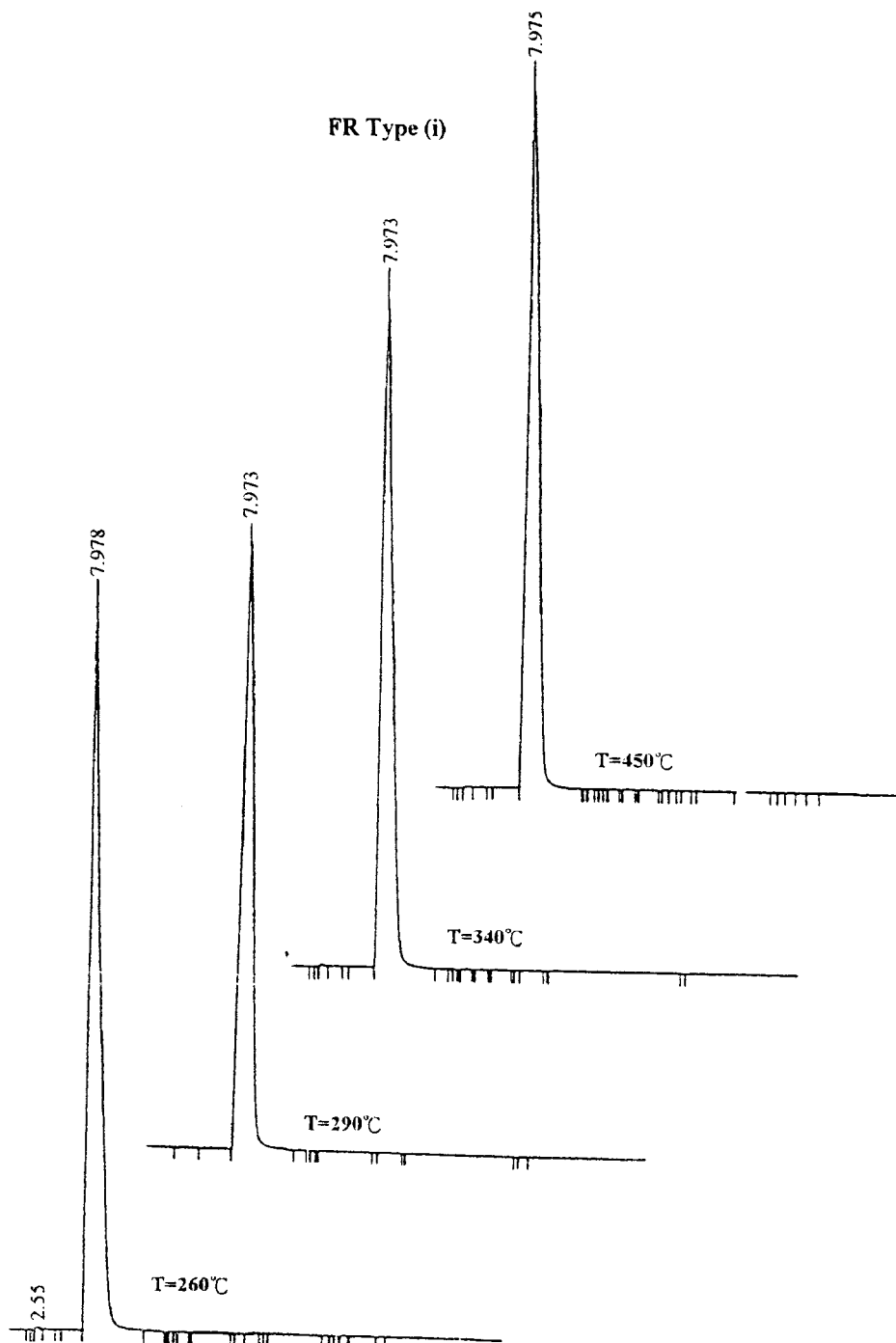


Figure 6 The GC profile of evolved-gases of product type (i) at different degradation temperatures for FR.

pylene. In addition, the FTIR spectra of the condensed phase at various temperature [Fig. 4(a)] indicate an isomerization reaction that occurred during the thermal degradation forming a more thermally stable structure, in which the $P=N$ bond changed into a $P-N$ bond.^{14,15}

The thermal degradation behavior of epoxy and its blends are one stage reaction. The temperature at which 5% mass is lost ($T_{5\%}$) and the peak temperature ($T_{d,max}$) at maximal degradation rate on DTG curve are lower for epoxy blends than for pure epoxy (Table II). By increasing FR

content the residual char yield of epoxy blends at 550°C increases also, but simultaneously the temperature ($T_{d,max}$) and maximal degradation rate of blends decrease.

Analysis of Evolved Gas

Analysis by TGA/FTIR

TGA/FTIR was used to characterize the pyrolysis gas of epoxy and its blends as shown in Figures 3 and 4. As shown in Figure 4(a), the FTIR spectrograms of the gas products of Ep0f at different degradation times (or temperatures) were similar. The major gas product at 38.0 min [Fig. 3(a)] is bisphenol A. The TGA/FTIR results of Ep2f are shown in Figures 3(b) and 4(b). The major gases evolved at 34.9 min were phenol and bisphenol A, identified by the assistance of the spectral databases. Additionally, the different characteristics of the FTIR peaks at various times (or temperatures) between Ep0f and Ep2f were as follows: (1) the intensities of the CH_3 and CH_2 bond at 2940, 2900, and 2850 cm^{-1} were scattered by adding of FR, and (2) the intensities of the benzene bond at 1600 and 1500 cm^{-1} and the ether bond at 1250 and 1180 cm^{-1} of Ep2f increased with the evolved time.

These results revealed that the addition of phosphorus compounds during the thermal degradation process would easily lead the scission of the C—C bond of bisphenol A.

Analysis by Pyrolysis/GC/MS

The pyrolysis temperatures of epoxy and its blend were determined on the basis of the initial temperatures and inflection points from TG curves. Therefore, the chosen pyrolysis temperatures of Ep0f were 300, 375, 400, 475, and 800°C, and for Ep2f were 250, 300, 340, 375, 400, 475, and 800°C. Figure 5(a) and (b) shows the pyrograms of Ep0f and Ep2f at different temperatures. Table III lists the volatile product species produced during the pyrolysis of the investigated samples and identified by their mass spectra and literature.^{1,11,12}

Figure 5(a) reveals that the peaks of Ep0f pyrograms were scattered within a pyrolysis temperature range of 300–400°C and the abundance of the peaks were obvious at above 400°C. While the major peaks at 10–16 min were assigned to higher phenol compounds such as (*o*, *m*, *p*)-cresols, (*o*, *m*, *p*)-isopropyl phenols, and (*o*, *m*, *p*)-ethyl phenols, the peaks from 23 to 28 min

were assigned to bisphenol A structure compounds. The bisphenol A structure appeared only at high temperature because bisphenol A, with a boiling point of 360.5°C (1.033 kg/cm^2),²² was accumulated in the link section between pyrolyzer and GC, and could not be carried out until the higher pyrolysis temperature was reached.

Ep2f pyrograms shown in Figure 5(b) can be divided into two groups: the one with pyrolysis temperature below 400°C and the major peak at 16.9–17 min, and the other one with the temperature above 400°C and the major peak at 10–11 min. While the peaks at 10–11 min were assigned to (*o*, *m*, *p*)-ethyl phenol compounds, the compound with the peak at 16.9–17 min and *m/e* of 183 was unidentified. The peak of bisphenol A appeared at high temperature also, but much smaller than that of Ep0f. The major differences of pyrograms between Ep0f and Ep2f were listed as follow: (1) both the scission behavior of the Ep0f and Ep2f systems would be accelerated with the increasing of pyrolysis temperature; (2) the thermal degradation temperature of the epoxy blends would be lower than that of pure epoxy. On the other hand, the addition of FR would accelerate the scission of epoxy resin; and (3) the amount of smaller molecules of the Ep2f system was greater than that of the Ep0f system. This phenomenon was due to FR with the electron withdrawing of the nitrogen atom that could attack and break the bisphenol A structure.

Analysis by Separation/GC/MS

This part will be focused on the analysis of the evolved gas, especially small molecules, using the separation/GC/MS during the thermal degradation process. Figure 6 shows the pyrograms for product type (i) of FR at different temperatures, while the pyrograms for product type (i) of Ep0f and Ep2f were not observed in these experiments. The spectra of the product type (i) of FR were found to contain a large amount of propylene, and this result correspond to our previous study.³

Figure 7(a) to (c) showed a series of GC traces at different temperatures representing product type (ii) gases of FR, Ep0f, and Ep2f, respectively. The product type (ii) gases of Ep0f and Ep2f consisted of mainly C1–C4, saturated, and unsaturated aliphatic hydrogen carbon compounds, and benzene. They were identified by ref. 13 and agreed with Cascaval's study.²¹ Additionally, the amount of the evolved products of FR, Ep0f, and Ep2f all increased with increasing temperature.

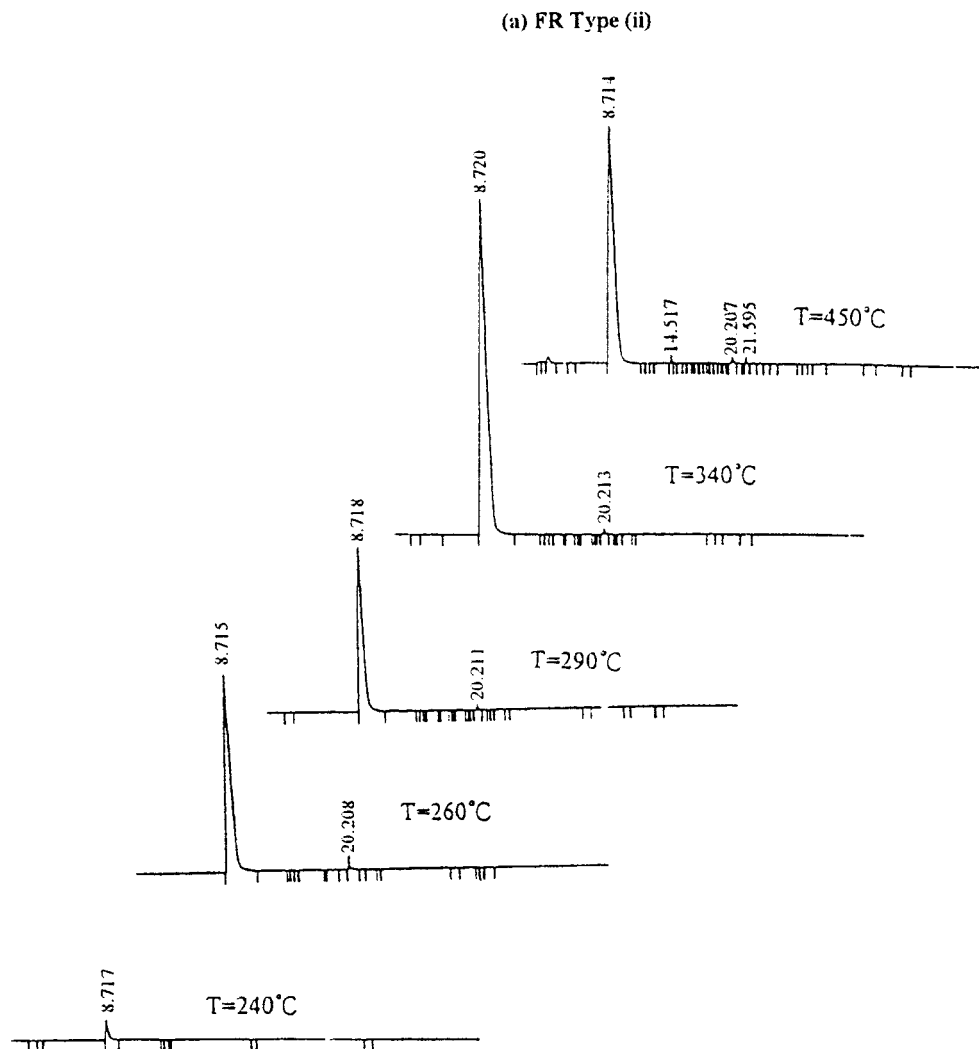


Figure 7 The GC profile of evolved gases of product type (ii) at different degradation temperatures for (a) FR, (b) Ep0f, and (c) Ep2f.

The major difference of the evolved gases product type (ii) between Ep0f and Ep2f was that the evolved product of pure epoxy at 9.3–9.4 and 13.3–14.5 min disappeared by addition of FR, and the new product of the blends at an evolved time of 8.9–9.0 min was produced.

Both Figure 8 and Table IV represented a GC/MS traces of the evolved gas of product type (iii) for FR, Ep0f, and Ep2f when samples were heated to a peak temperature of the DTG curve at the heating rate of 10°C/min. The evolved products of FR at various evolved times were identified to be acetone, *N*-propanamine (or dipropyl ether), and tributyl ester phosphoric acid by the spectra data library. The major evolved type (iii) products of Ep0f and Ep2f included acetone,

1-propanol, 2-propanol, phenol, (*o*, *m*, *p*)-isopropyl phenol, and (*o*, *m*, *p*)-isopropylenyl 2,4-cyclohexidenone.

The major differences of evolved type (iii) between Ep0f and Ep2f were stated as follow: (1) The formation of 1-propanol and 2-propanol was only observed during thermal degradation of epoxy by adding of FR. (2) All of the amount of acetone, phenol, and isopropyl phenol produced by Ep2f were greater than those of Ep0f.

The above phenomena was due to FR released propylene during the thermal degradation process, and its residual char contained an active proton to attack the 4,4-isopropyl phenol, ether group, and C—N bond. Therefore, phenol, isopropyl phenol, and propyl radicals were produced.

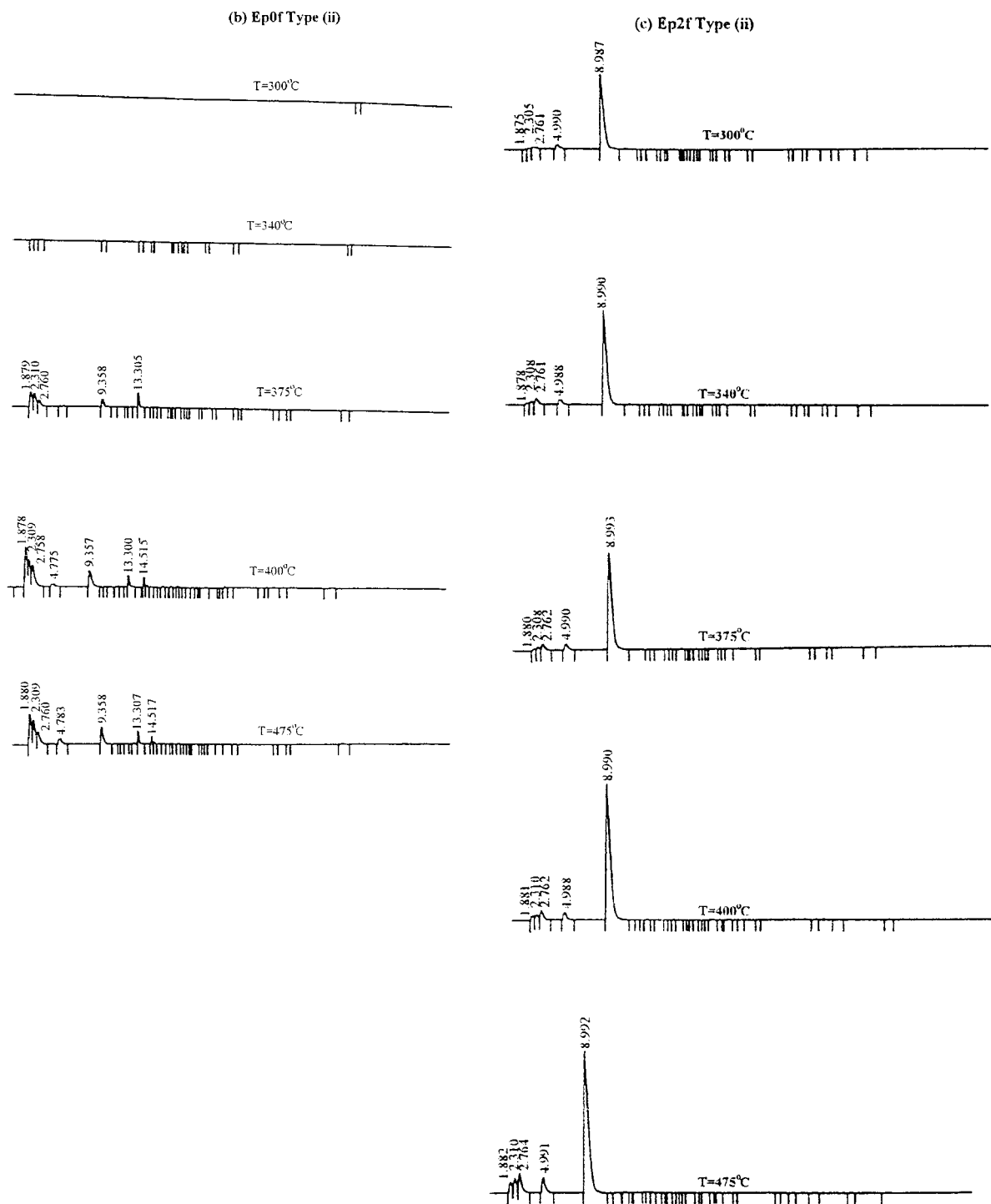


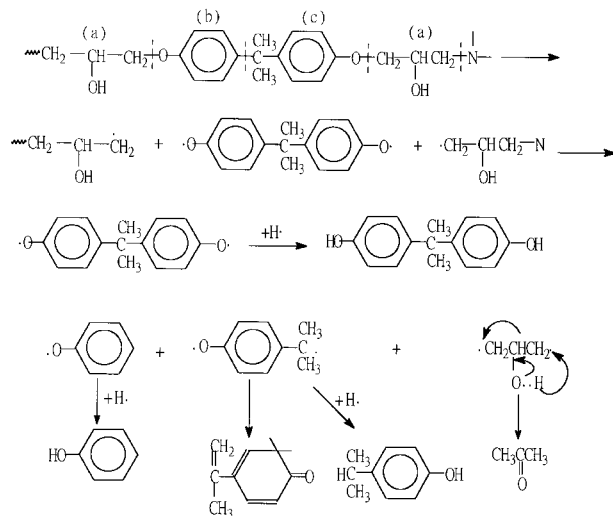
Figure 7 (Continued from the previous page)

The propyl radical reacts then with the residual char to form 1-propanol, 2-propanol, and acetone through many complex reactions.¹⁶ Additionally, the sources of a large amount of acetone, phenol, and isopropyl phenol were also due to an active

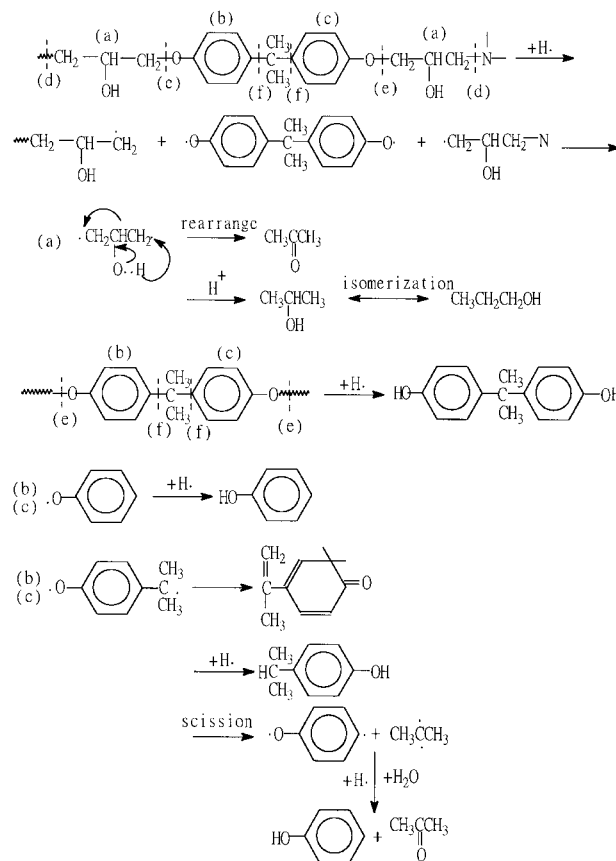
proton from FR easily attacked bisphenol A structure.

From the evolved substances in the experiments, our previous study,¹⁶ and literature,^{1,11,12} the pyrolysis mechanism of pure epoxy resin and

its blends were proposed to be as follows: (a) pyrolysis mechanism of epoxy resin



(b) pyrolysis mechanism of epoxy resin blended with FR.



Analysis of Residual Char Yield

The FTIR spectra of the condensed phase of epoxy and its blends at various temperatures (with a

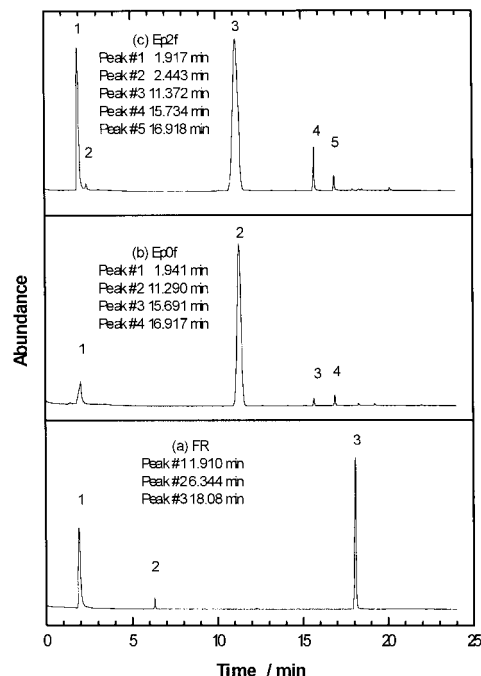


Figure 8 The GC profile of evolved gases of product type (iii) for (a) FR, (b) Ep0f, and (c) Ep2f.

heating rate of 10°C/min under nitrogen atmosphere) were shown in Figure 9(a) and (b), respectively. The intensities of peaks at 1600 and 1500 cm^{-1} , assigned to resulting from benzene ring of Ep0f, decrease with the increase of temperature, as shown in Figure 9(a). Additionally, two of three absorption peaks, one at 1250 cm^{-1} due to the Ar—O group and the other at 1040 cm^{-1} due to the C—O group, disappeared at 550°C. Finally, the peaks at 2940, 2900, and 2850 cm^{-1} , resulting from methyl and methylene, disappear at 550°C. But it is worth noticing that the bands at 810 cm^{-1} due to the out of plane C—H bending of the *p*-substituted aromatic ring disappeared at 550°C, and peaks 9 and 10 due to the out-of-plane C—H vibration of honeycomb compounds^{20,21} developed.

In the FTIR spectra of Ep2f [Fig. 9(b)] it is evident that all of the signals such as Ar—O, C—O, benzene ring, methyl, and methylene disappeared at 400°C, and the out-of-plane C—H vibration of honeycomb structure became evident and broad. The band broadness may be the result of phosphorus compound bonds such as P—O—(C) (830–740 cm^{-1}), (P)—O—C (1050–970 cm^{-1}), P—OH (1040–910 cm^{-1}), and P—N (1100–930 cm^{-1}), respectively. From the analysis of evolved gas and the increase of the residual

Table IV Species of Product Type (iii) of Thermal Degradation of Epoxy Resin and Its Blends Identified by Mass Spectra

Sample Code	Evolved Time (min)	Assignment	<i>m/e</i>
FR	1.910	Acetone	58
	6.344	<i>N</i> -propyl-1-propanamine	101
		or	or
Ep0f	18.08	Dipropyl ether	102
	1.941	Tributyl ether phosphoric acid	206
	11.290	acetone	58
	15.691	phenol	94
	16.917	(<i>o, m, p</i>)-isopropyl phenol	136
EP2F	16.917	(<i>o, m, p</i>)-isopropylene 2,4-cyclohexidenone	134
	1.917	acetone	58
	2.443	1-propanol	60
		or	or
		2-propanol	60
	11.372	phenol	98
	15.734	(<i>o, m, p</i>)-isopropyl phenol	136
16.918	(<i>o, m, p</i>)-isopropylenyl 2,4-cyclohexidenone	134	

char yield, it seem that the epoxy and its blends are split off and the honeycomb structure forms with the increase of temperature. Additionally, the scission of epoxy and the formation of honeycomb structure are easier when adding the FR than without it. The phosphorus atom remains in the residual char yield of Ep2f.

Elemental Analysis

To understand the proportion of residual content of various elements relative to the initial state (25°C), the ratio, *R*, was defined:

$$R = \frac{(\text{content at any temperature for element } i) * (1 * \alpha_T)}{(\text{content at } 25^\circ\text{C for element } i)} \quad (1)$$

where α_T is the weight loss fraction of sample at temperature *T*.

Figure 10 showed the variation of this ratio for various elements relative to the weight loss fraction of Ep0f and Ep2f. It could be seen that the carbon, hydrogen, oxygen, and nitrogen atoms were being lost steadily throughout the heating process, but most of the amount of phosphorus atom remained in the residual char yield. This phenomena was also observed in Weil,¹⁸ and Li's¹⁹ studies. FTIR analysis of the residual char in this article also showed that phosphorus could function in the condensed-phase to form char.

The Interaction between Epoxy Resin and FR During Pyrolysis Process

The above evidences revealed that addition of FR would accelerate the scission of epoxy and form new honeycomb structure compounds. To examine the degree of interaction between epoxy and FR during the thermal degradation of epoxy blends, a mixing rule that assumed no interaction effect, was employed:

$$W_{\text{blend}} = W_{\text{Ep}} \cdot X_{\text{Ep}} + W_{\text{FR}} \cdot X_{\text{FR}} \quad (2)$$

where W_{blend} is the residual weight fraction of epoxy blend at temperature, *T*; W_{EP} and W_{FR} are the residual weight fractions of pure epoxy resin and of FR at temperature, *T*; X_{EP} and X_{FR} are the weight fractions of pure epoxy resin and of FR, respectively. Figure 11 shows the comparison of the experimental TG curves and the TG curves calculated according to the mixing rule. They did not match, because the mixing rule showed a two-stage reaction while the experimental results show a one-stage reaction. In addition, the experimental weight loss fractions are smaller than those calculated for the first stage from the mixing rule, while for the second stage that is opposite. The experimental residual char yield at 550°C is higher than the results calculated from mixing rule. Therefore, it can be concluded that the interaction between FR and epoxy does exist

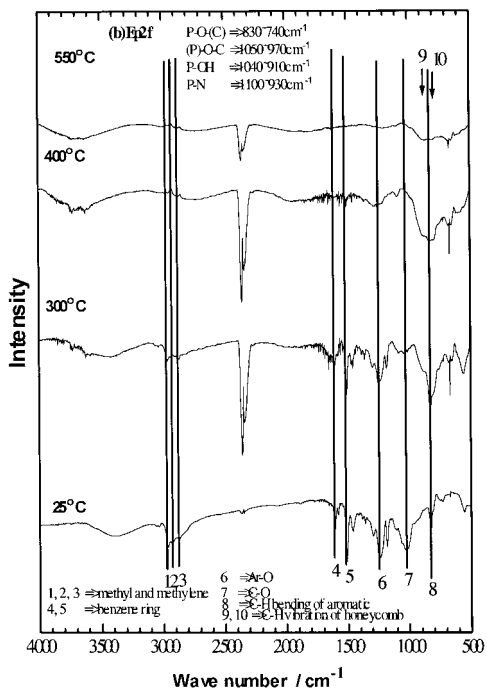
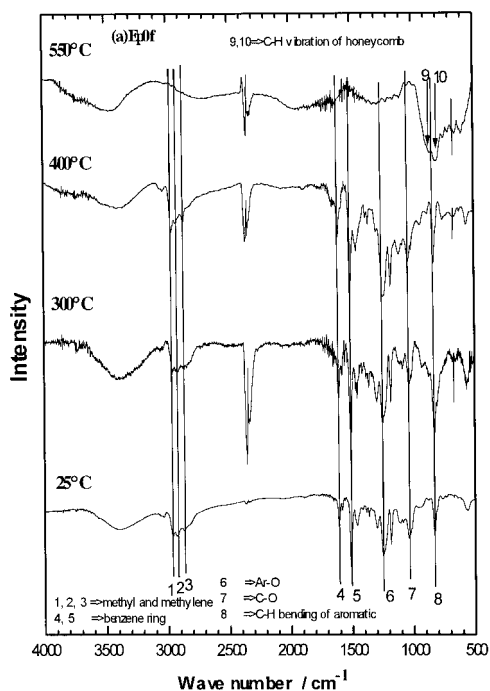


Figure 9 FTIR spectra of condensed phase in thermal degradation at various temperatures for (a) Ep0f and (b) Ep2f.

during the thermal degradation process and corresponds with the above experiments.

CONCLUSION

From this study, several conclusions could be made:

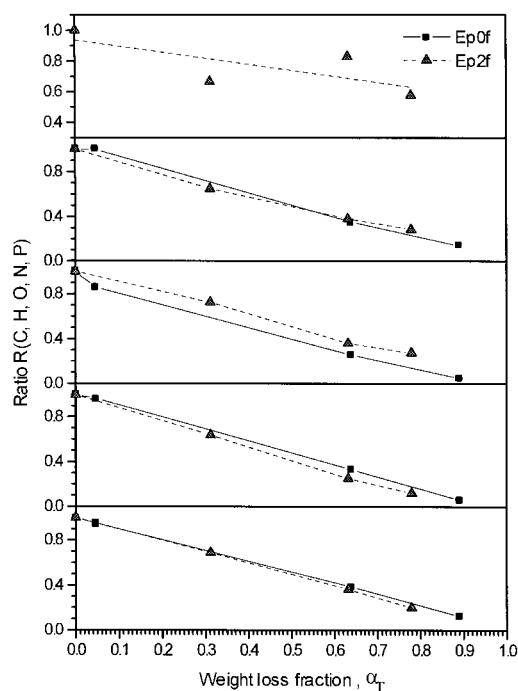


Figure 10 Variation of ratio R(C, H, O, N, P) with weight loss fraction (α_T) for Ep0f and Ep2f.

1. The thermal degradation of epoxy resin and its blends was a one-stage reaction.
2. FR reduced the major degradation temper-

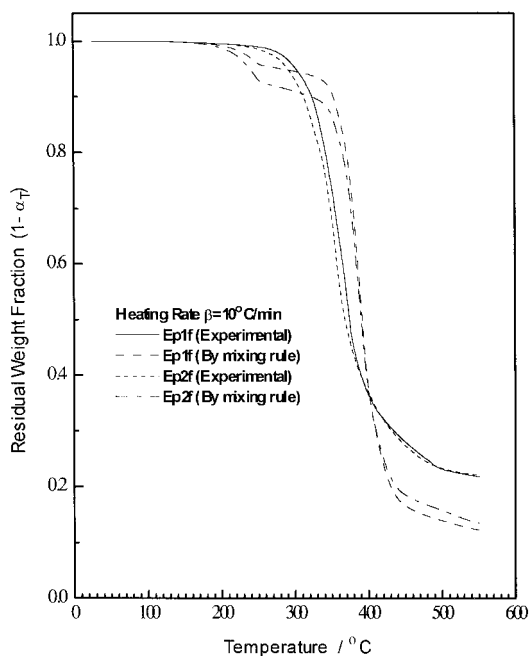


Figure 11 Comparison of experimental TG thermogram and thermogram calculated according to the mixing rule for Ep1f and Ep2f.

ature of the blends relative to pure epoxy resin, and also accelerated the scission of epoxy resin. There were a large amount of liquid products such as acetone, phenol, and isopropyl phenol that evolved during thermal degradation. Additionally, FR accelerated the formation of carbonaceous char, and thus increased the residual char at 550°C.

3. The major evolved gas of epoxy resin and its blends formed during the early thermal degradation were bisphenol A and higher phenol compounds. The bisphenol A originates from the scission of the C—O bond of the ether group. By increasing the temperature, the bisphenol A could break into a variety of small molecules such as phenol and isopropyl phenol.
4. The evidences of elemental analysis and infrared spectra of the residual char showed that phosphorus was a residual element, while the other elements mostly diffused to the evolved gas. Additionally, the scission of epoxy and the formation of honeycomb structure are easier by adding the FR than without it.

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