

Novel thermosetting resins based on 4-(*N*-maleimido)phenylglycidylether III. Studies on the thermal degradation kinetics and mechanisms of the cured resins

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Abstract

The thermal degradation kinetics and mechanisms of thermosetting resins based on 4-(*N*-maleimido)phenylglycidylether (MPGE) were investigated with TGA, GC/MS, and FTIR. Two samples from MPGE cured with 4,4'-diaminodiphenylmethane (DDM) and diethylphosphite (DEP), respectively, were studied. The MPGE based resins showed good thermal stability over conventional epoxy resins. The degradation of MPGE–DEP was found to be initially triggered at the phosphonic ester linkage, while MPGE–DDM reacted at the epoxy linkage. Introducing phosphorus therefore significantly altered the patterns, activation energies, and mechanisms of the degradation reactions of the MPGE resins. This change caused the MPGE–DEP resin to show good thermal stability, high activation energies of degradation, and enriched char formation.

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1. Introduction

Thermosetting polymeric materials, including addition polyimides and epoxy resins, are used as matrix resins for high performance composites based on glass-, carbon-, and aramid fibres [1]. The applications of such resins are also for electronic/electrical materials such as printed circuit boards and insulators. To obtain a material possessing a balance of the properties of polyimides and epoxy resins, some efforts have been made to combine the versatility of these two resins [2–7]. The

approaches included forming epoxy resin-polybis-maleimide interpenetrating networks (IPN) [2,3], curing epoxy resins with agents containing imide groups [4,5], and blending epoxy resins with thermoplastic polyimides or functional polyimides [6,7].

With our continuing efforts on developing high performance thermosetting materials, maleimide and epoxy structures were put together by synthesizing a hybrid monomer of 4-(*N*-maleimidophenyl)glycidylether (MPGE) and its cured resins [8]. The cured resins showed high glass transition temperatures, excellent thermal stability, and attractive flame retardance, suggesting potential uses as matrix and encapsulants in advanced application in aerospace, electrical, and electronic industries. In this work the thermal degradation kinetics and mechanisms of the MPGE based resins were

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studied to provide a better understanding of the characteristics of the resin behaviour under heat and fire.

Thermogravimetric analysis is widely used in evaluating the thermal degradation kinetics of polymeric materials [9–17]. With some process techniques, such as Coats–Redfern method [18], Kissinger method [19], Friedman method [20], and Ozawa method [21], the TGA analysis results can provide some parameters of the degradation kinetics. On the other hand, several techniques, such as gas chromatography [22], mass spectroscopy [23,24], Fourier-transform infrared [25–27], or combinations of these [28–30] have been used to study the degradation mechanisms of polymeric materials. In the current work, both evolved gas analysis and substrate evaluation were carried out by means of TGA–GC/MS and temperature-resolved FTIR, respectively, to study the degradation mechanisms of the MPGE based cured resins.

2. Experimental

2.1. Materials

4-(*N*-maleimido)phenylglycidylether (MPGE) and the resins cured with 4,4-diaminodiphenylmethane (DDM) and diethylphosphite (DEP) were prepared in the laboratory according to the reported procedures [1]. The chemical structures of the compounds used are shown in Fig. 1.

2.2. Instruments

Thermogravimetric analysis was performed with a Thermal Analysis TGA-2050. FTIR spectra were recorded with a Nicolet 330 FTIR accessed with a heating stage and high temperature cell. Evolved gas analysis was performed by collecting the evolved gases from a TGA (Perkin–Elmer TGA 7, at a heating rate of 10 °C/min under helium flow of 100 mL/min) by an automatic thermal desorption instrument (Perkin–Elmer ATD 400). The collected gases were then transferred to a hyphenated GC/MS (Clarus 500 GC/Clarus 500 MASS with electron ionisation, 120 V). The desorption was performed at 250 °C with a helium flow of 30 sccm. The heating program for the GC analysis is from 40 °C (inlet temperature) to 250 °C at a heating rate of 10 °C/min, then isothermal at 250 °C till the analysis is complete.

3. Results and discussion

3.1. Thermal degradation kinetics from TGA data

Fig. 2 shows the TGA and DTA thermograms of the investigated resins both in nitrogen and air atmosphere

[8]. For MPGE–DDM, the weight loss rate at around 400–450 °C in air was relatively slower than that in nitrogen. Oxygen might take part in the degradation reactions of MPGE–DDM, i.e. the thermal-oxidative degradation, to retard the degradation rate through adding weight with oxidation and/or forming thermally stable residues. On the other hand, the above-mentioned behaviour was not observed with MPGE–DEP. The weight loss rate of MPGE–DEP at about 400–450 °C was slower than that of MPGE–DDM, both in nitrogen or in air. The phosphorus (from DEP) in MPGE–DEP played a critical role in forming phosphorus-rich char in the degradation of MPGE–DEP. The phosphorus-rich char was more thermally stable to show the retarded weight loss patterns for MPGE–DEP. Rapid weight loss occurring at temperatures of 500–600 °C was observed for both resins in air, and this weight loss was correlated to oxidative degradation of the formed char. The great oxidative stability of the char of MPGE–DEP was noteworthy with the high char yield of MPGE–DEP at high temperatures. The thermal stability and degradation behaviour of the MPGE based resins were also examined with isothermal TG analysis at 320 and 400 °C (Fig. 3). While heated in nitrogen at 320 °C, MPGE–DEP showed its excellent thermal stability, only losing about 7 wt% in 500 min. The weight loss of MPGE–DEP heated at 400 °C for 500 min was only about 20%. From the isothermal TG analysis it was also seen that MPGE–DEP showed relatively good thermal stability, both in nitrogen and air. The retarded weight loss behaviour for MPGE–DDM heated in air, compared with that in nitrogen, was also observed with samples heated at 320 °C. However, this behaviour vanished for the resin heated at high temperature.

Studies on the kinetics of the thermal degradation of MPGE resins were conducted with TG analysis at various heating rates of 5, 10, 15, 20 and 25 °C/min. Two calculation methods, proposed by Ozawa [21] and Kissinger [19], respectively, were used to determine the activation energies of the thermal degradation reactions. Typical plots of these two analysis approaches are shown in Fig. 4 (Kissinger method) and Fig. 5 (Ozawa method). Table 1 collects the calculated data of the activation energies from Kissinger's method. While heated in nitrogen, MPGE–DDM showed an activation energy of 245 kJ/mol, which was much higher than the E_a of decomposition of bisphenol-A type epoxy resins (around 160 kJ/mol [30]), and was similar to the decomposition E_a of maleimide resins (around 254 kJ/mol [17]). The E_a value of MPGE–DDM also implies that the highly thermal stability was from the maleimide groups and the degradation of epoxy and maleimide linkages of the resin were involved in a one-spot mechanism. The relatively low E_a of MPGE–DDM heated in air indicated that this resin was easily

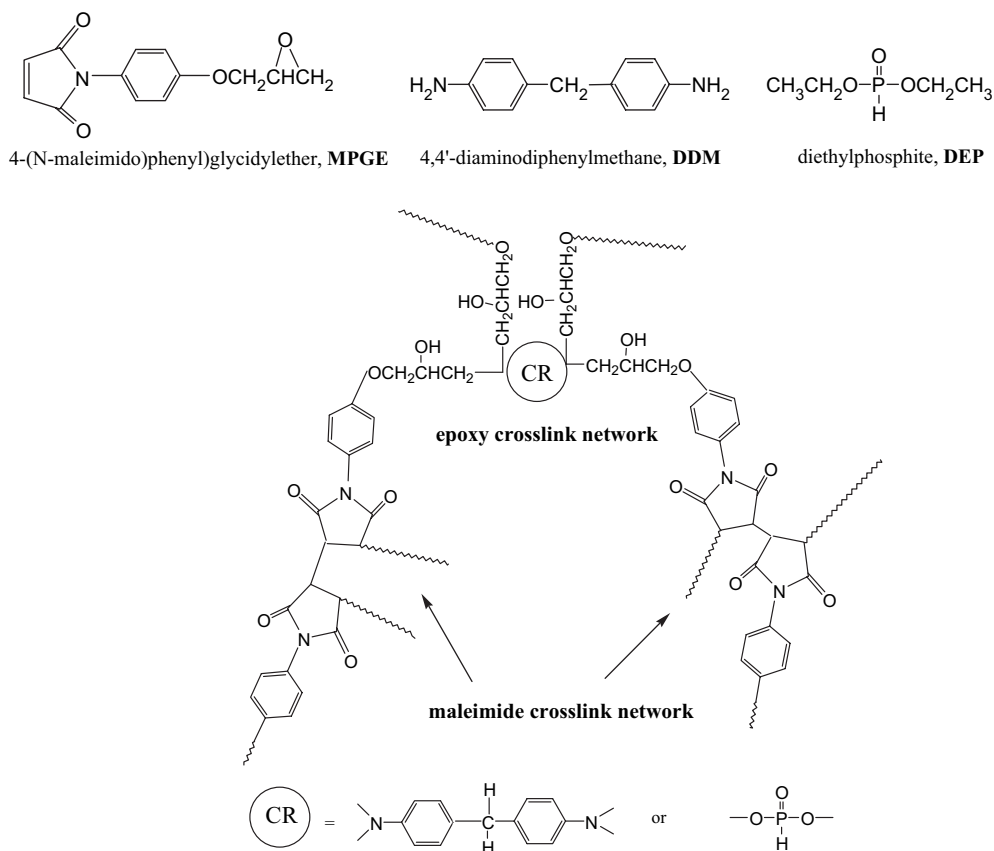


Fig. 1. Chemical structures of the curing monomers and cured resins.

undergoing thermal-oxidative degradation. On the other hand, MPGE–DEP showed various activation energies of its degradation reactions. The pre-stage degradation, which was not observed with MPGE–DDM, was correlated to the decomposition from the P–O and

P–C linkage [9,30]. However, compared with other phosphorus-containing polymers [9,15,27,29,30], the activation energy of the pre-stage degradation of MPGE–DDM was relatively high. The E_a of first stage degradation of MPGE–DEP was also higher than that

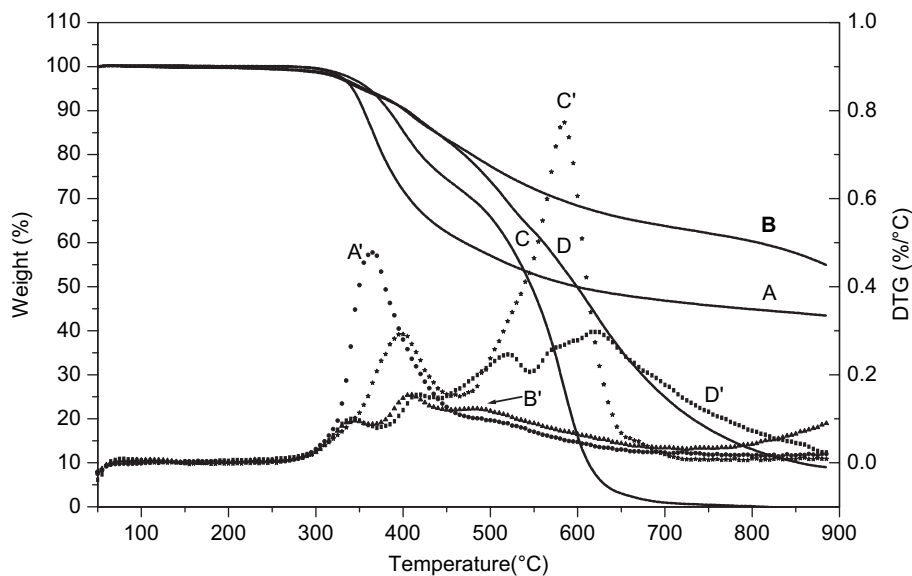


Fig. 2. TGA (curves A–D) and DTG (curve A'–D') thermograms of the MPGE cured resins. A, A': MPGE–DDM in N_2 ; B, B': MPGE–DEP in N_2 ; C, C': MPGE–DDM in air; D, D': MPGE–DEP in air.

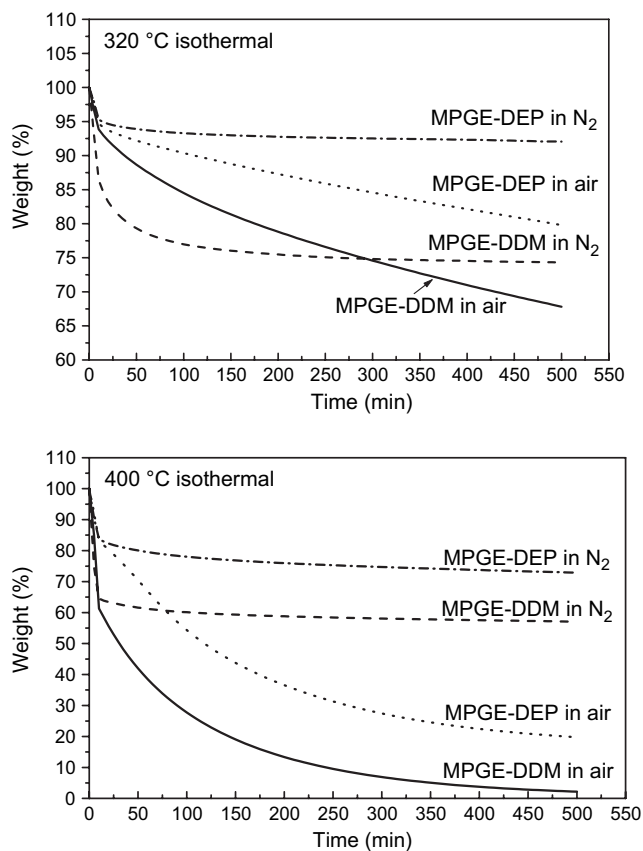


Fig. 3. Isothermal TGA thermograms of MPGE cured resins at 320 °C (left) and 400 °C (right).

of MPGE-DDM, to denote that the residue from the pre-stage weight loss of MPGE-DEP was more thermally stable. This result was coincident with the results revealed from isothermal TG analysis.

The kinetic data calculated from Ozawa's method, which provide the relationship of the conversions and activation energies, are listed in Table 2. The fitting straight lines in Fig. 5 showed four parallel groups, thus

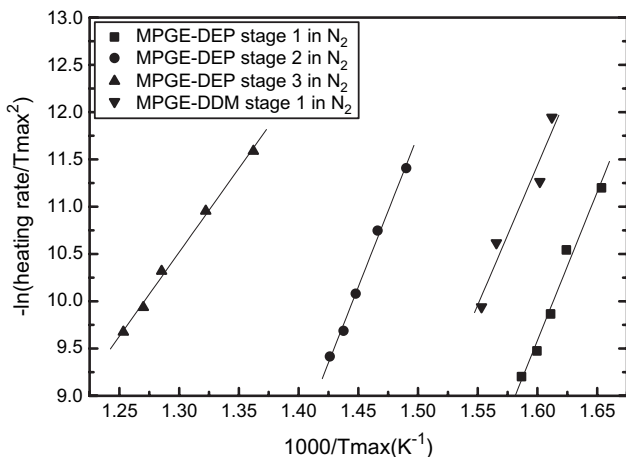


Fig. 4. Determination of activation energies of the degradation reactions of MPGE resins through Kissinger's method.

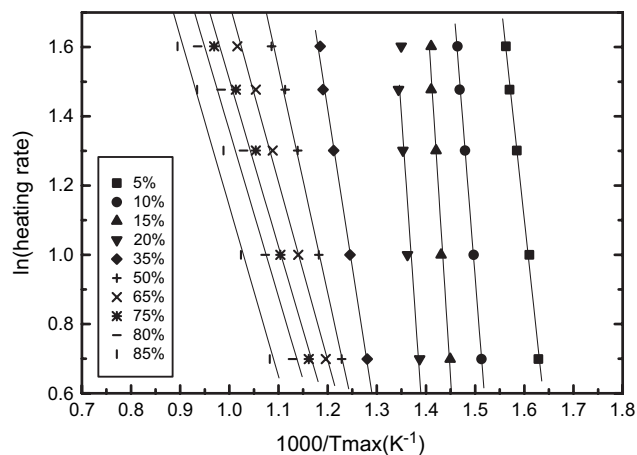


Fig. 5. Determination of activation energies of the degradation reactions of MPGE-DEP in air through Ozawa's method at various conversions.

indicating that the thermal-oxidative degradation of MPGE-DEP should involve a 4-step mechanism [15] at the conversions of 0–5%, 5–20%, 20–50%, and 50–85%. It can be seen that the data from the Ozawa method showed similar results as that from Kissinger's method. Moreover, the dependence of the activation energy on the degree of conversions is shown in Fig. 6 [31]. It was reported that polymers containing flame retardants showed high energy barriers at high conversions [31]. Generally, phosphorus-containing polymers were considered as highly flame retardant. However, in this study the energy barriers for MGPE-DDM and MPGE-DEP were not so obviously different. This might be due to the imide structure often also expressing certain efficiency in enhancing the flame retardant property of polymers.

3.2. FTIR analysis on thermal degradation mechanisms

FTIR was first applied to monitor the thermal-oxidative degradation of the MPGE based resins. The temperature-dependent FTIR spectra (from 150 to

Table 1
The activation energies of the degradation reactions from Kissinger's method

Sample	Degradation stage	In N ₂		In air	
		E_a (kJ/mol)	R^a	E_a (kJ/mol)	R^a
MPGE-DDM	I	245	0.9706	130	0.9994
	II	—	—	90	0.9919
MPGE-DEP	Pre	260	0.9888	220	0.9981
	I	270	0.9975	255	0.9939
	II	140	0.9993	140	0.9902
	III	—	—	125	0.9805

^a Correlation coefficient.

Table 2
The activation energies of the degradation reactions at various conversions from Ozawa's method

Atmosphere	Conversion (%)	MPGE-DDM		MPGE-DEP	
		E_a (kJ/mol)	R^a	E_a (kJ/mol)	R^a
In N ₂	5	220	0.9968	230	0.9860
	10	230	0.9920	305	0.9690
	15	250	0.9805	230	0.9964
	20	280	0.9704	230	0.9994
	35	—	—	335	0.9988
In air	5	240	0.9821	240	0.9978
	10	290	0.9695	330	0.9988
	15	400	0.9790	370	0.9926
	20	—	—	330	0.9784
	35	—	—	165	0.9972
	50	150	0.9864	120	0.9983
	65	120	0.9895	95	0.9967
	75	110	0.9952	90	0.9927
	80	105	0.9963	90	0.9867
	85	100	0.9974	90	0.9851
	90	100	0.9981	—	—

^a Correlation coefficient.

470 °C with a heating rate of 10 °C/min) of these two resins, MPGE-DDM and MPGE-DEP, are shown in Figs. 7 and 8, respectively. The spectra were recorded at every 20 °C temperature increase. It can be seen that below 300 °C the spectra did not undergo extensive changes, reflecting that there was no obvious change in the molecular structure of the resin network. While samples were heated at above 430 °C, the spectral features of the residuals were seriously changed, implying that the structure of the resin network was destroyed. For MPGE-DDM (Fig. 7), the broad band centred at about 3335 cm⁻¹ (—OH group) and the peak at 2922 cm⁻¹ (—C—H stretching) showed decrease in intensity with increasing temperatures. The absorption peak at 1075 cm⁻¹, which is due to a C—C—O vibration mode of the secondary alcohol, also decreased substantially at temperatures higher than 370 °C. These peak changes suggested the MPGE-DDM resin initially

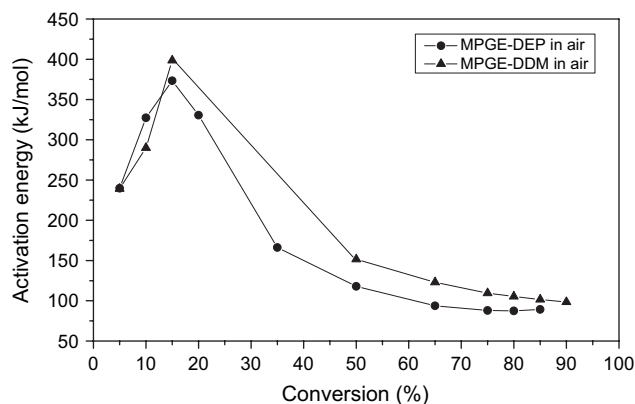


Fig. 6. The plots of activation energies vs. conversion based on Ozawa's method.

degraded at the —C—C(OH)—C— linkages. It was suggested that the secondary alcohol structure of an epoxy resin might degrade through a dehydration reaction to form C=C bonds [30,32,33] or through a thermally oxidative reaction to form a peroxide group [25,34]. However, the absorbance strength of the peroxide group (at around 831 cm⁻¹) did not show increases in the period of heating. On the other hand, the C=C absorption at about 1647 cm⁻¹ was indeed observed with temperature increases, in spite of the peak overlapping with the absorption peak of C=O at 1713 cm⁻¹ and only clearly observed at temperatures above 450 °C. Moreover, the absorption bands centred at 1779 cm⁻¹ (symmetrical vibration of —C=O), 1713 cm⁻¹ (asymmetrical vibration of —C=O) and 1341 cm⁻¹ (C—N—C) did not show any significant change in peak position or absorbance at temperatures below 410 °C, implying that the maleimido-structure of the MPGE-DDM might be thermally stable at such high temperatures.

Fig. 8 shows the FTIR spectra at various temperatures of the other resin of MPGE-DEP. With temperature increasing, the broad band centred at 3480 cm⁻¹ (—OH group) showed change in shape from broad to sharp and peak shift to 3500 cm⁻¹. This peak shift might come from breaking the hydrogen bonding between the phosphonate and hydroxyl groups, owing to the degradation of the phosphonic ester linkages. The peaks at 2945 (—CH₂— vibration) and 2890 cm⁻¹ (C—H vibration, secondary alcohol) also exhibit decrease in intensity. The above-mentioned dehydration of the secondary alcohol could be also applied to interpret the MPGE-DEP degradation. However, the degradation of the phosphonic ester structure (—P(O)—O—C—) in the MPGE-DEP resin also accompanied the dehydration reaction. The occurrence of the degradation reaction at the phosphonic ester structure was also observed from the absorbance change at 1020 cm⁻¹ (P—OH, absorbance increase) and 1262 cm⁻¹ (—P=O in phosphonic ester, absorbance decrease). Moreover, the absorbance at 1100–1300 cm⁻¹ was decreased obviously for MPGE-DEP. However, this behaviour was not observed for MPGE-DDM. Moreover, for MPGE-DEP, the absorption bands corresponding to the maleimido-structure clearly exhibited changes at temperatures below 430 °C. The absorbance of C=O and C—N—C groups decreased and the peak of C—N—C group shifted to lower wavenumber. The above spectral changes show that the maleimido-structure of MPGE-DEP network degraded during heating at temperatures above 350 °C, in spite of the fact that for MPGE-DDM these absorption peaks did not exhibit alteration below 430 °C. This phenomenon was explained as follows. The phosphonic ester structure (from the curing reaction of epoxy and phosphite groups) in the MPGE-DEP resin was considered as relatively thermally

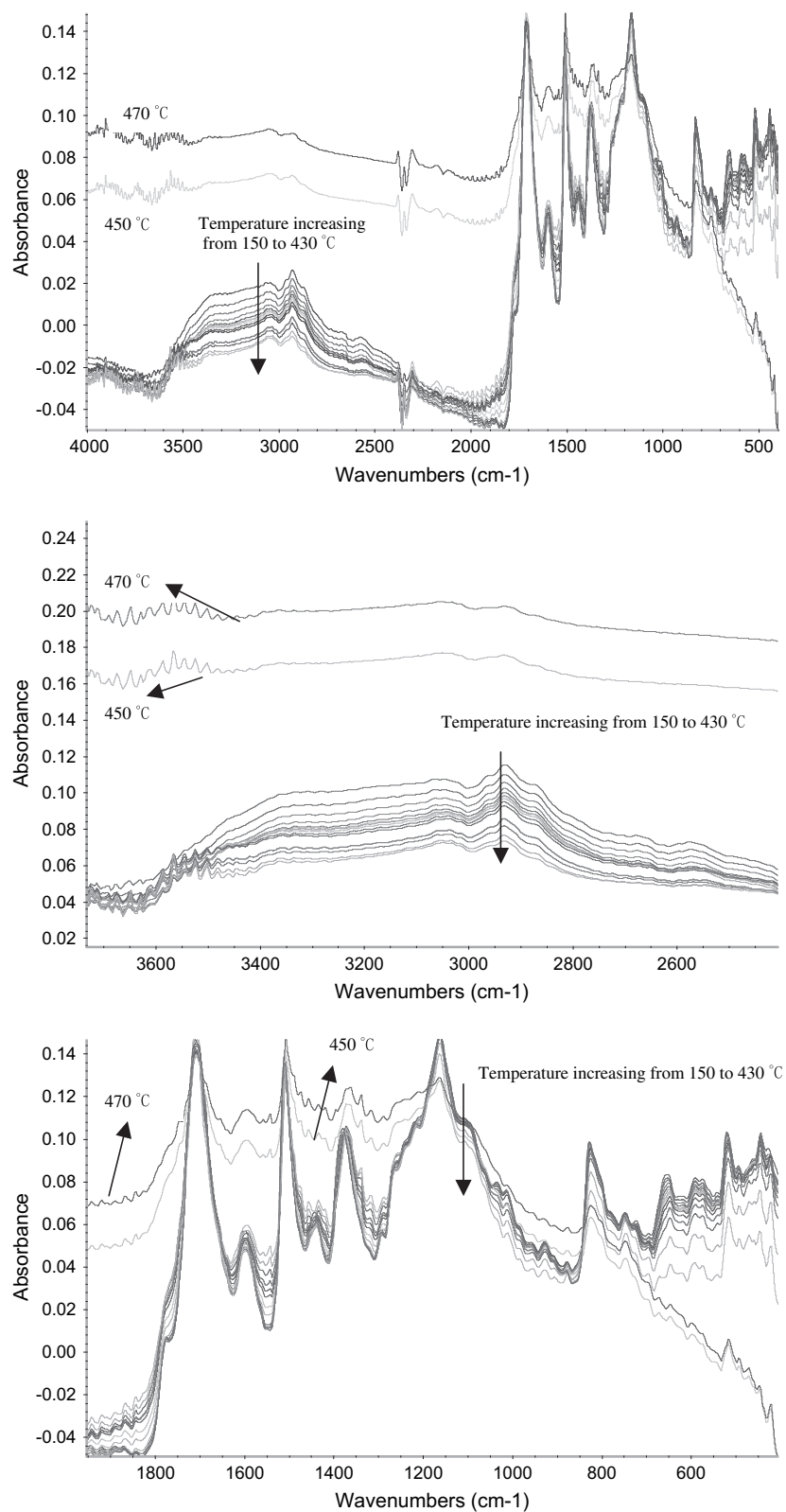


Fig. 7. FTIR spectra of MPGE-DDM collected at various temperatures during heating process (150–470 °C). Spectra were taken at every 20 °C temperature increase.

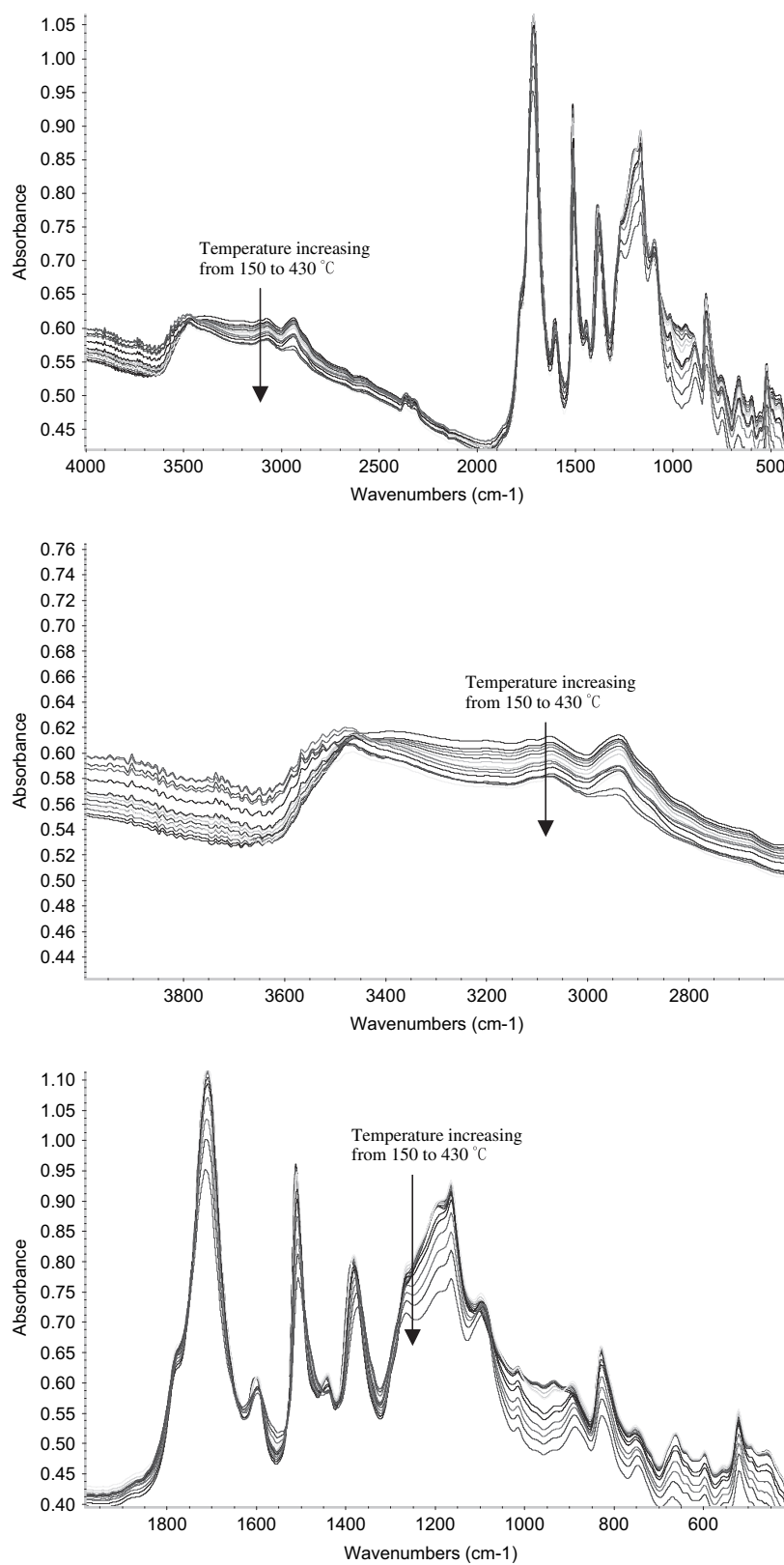


Fig. 8. FTIR spectra of MPGE-DEP collected in various temperatures during heating process (150–430 °C). Spectra were taken at every 20 °C temperature increase.

unstable to degradation at low temperature region (around 300 °C). The degradation of phosphonic esters formed phosphonic acid group, which induced the degradation of the maleimido-structures through an acid-catalysed carbonation mechanism [35].

3.3. TGA–GC/MS analysis on thermal degradation mechanisms

The degradation reaction of the MPGE based resins was further characterized by means of evolved gas

analysis. The sample was heated under programmed process in a thermogravimetric analyser, and the evolved gases were collected with a thermal desorption instrument at different temperature ranges. The collected gases were identified by GC/MS. Fig. 9 shows the typical chromatograms of the evolved gases from the degradation of MPGE resins. The identified chemicals of the evolved gases from the thermal degradation of MPGE resins are shown in Table 3. Small amounts of evolved gases were detected for MPGE–DEP in the temperature range of 250–350 °C, to indicate that

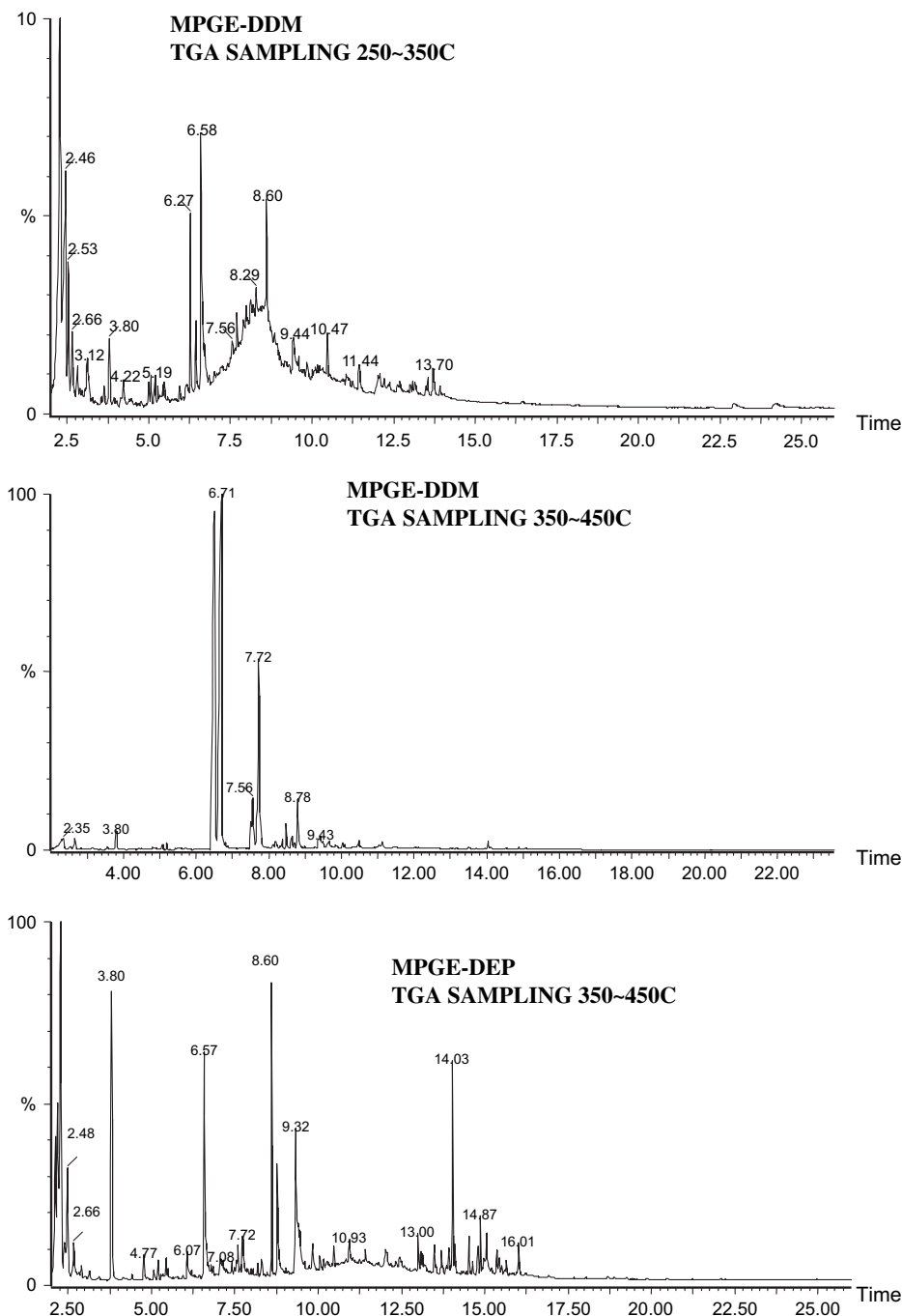
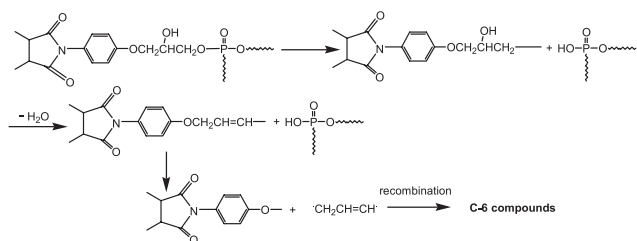


Fig. 9. The GC chromatograms of the evolved gases from TGA.

MPGE–DEP was thermally stable in the temperature range. The major products of MPGE–DEP degradation found in this stage were C₆ isomers, including 2-methylpentane, 3-methylpentane, methylcyclopentane, and hexane etc. The above results imply that the degradation of MPGE–DEP initially occurred at the epoxy linkage and the mechanism could be proposed below. In spite of the fact that the dehydration reaction of the secondary



alcohol is widely observed for the degradation of epoxy resins, it is reasonable to believe that this reaction occurred more easily in MPGE–DEP with catalytic effect of the phosphonic groups. Another degradation route beginning at the cleavage of the ether linkage was observed in the degradation of epoxy resins with the formation of acetic acid, which was observed for both MPGE–DDM and MPGE–DEP.

On the other hand, much larger amounts of evolved gases were detected for MPGE–DDM degradation at 250–350 °C. In addition to 3-methylpentane, considerable amounts of acetic acid, toluene, isocyanatobenzene, aniline, phenol, and other high molecular weight aromatic derivatives were found in the evolved gases. The relatively small amounts of the C₆ compounds and the appearance of acetic acid in the evolved gases implied the degradation of MPGE–DDM started partly with the cleavage of the ether linkage of the epoxy groups and partly with the dehydration reaction of the secondary alcohol. Furthermore, it is noteworthy that aromatic compounds were observed in this stage of degradation of MPGE–DDM. These might be reasonably derived from the degradation of the maleimidophenylether and DDM structures. The occurrence of recombination reactions of the degradation products resulted in high molecular weight chemicals. Generally, a phosphorus-containing epoxy resin was considered to be less thermally stable, and the initial degradation products of the phosphorous epoxy resin were usually from the phosphorous groups. However, for MPGE–DEP, there are no thermally unstable groups pendent with the phosphorus groups. The degradation at the phosphorus groups formed phosphonic acid without any accompanying weight loss. This could be an explanation for the relatively good thermal stability of MPGE–DEP and other DEP cure epoxy resins [36].

From the above discussion it is suggested that at 250–350 °C the major structure of the resin network

disintegrated for MPGE–DDM and not for MPGE–DEP. The alternation of the initial degradation behaviour led to very different results of the following degradation behaviour at high temperature. For MPGE–DDM, the major degradation products at temperatures between 350 and 450 °C were aniline, phenol, and their derivatives such as methylphenol, aminotoluene, ethylphenol, and ethylaniline. The phenol derivatives were from the maleimidophenylether structure of MPGE and the aniline derivatives from the aminophenyl structure of DDM. The structure of MPGE–DDM was thoroughly destroyed in this temperature region. For MPGE–DEP at temperatures between 350 and 450 °C, the observation of some aromatic compounds, including toluene, phenol, and phenol derivatives, in the evolved gases indicated the occurrence of decomposition reactions at the maleimidophenylether structure. However, some aromatic derivatives with cyclic aliphatic structure and high molecular weights, which did not appear in the evolved products of the MPGE–DDM degradation, were observed with MPGE–DEP. These aromatic compounds were probably formed by some recombination reactions of the degradation products and dehydration reactions catalysed with the formed phosphonic acid. Moreover, it was noteworthy that no nitrogen-containing and phosphorus-containing compounds were detected in the degradation products of MPGE–DEP. This result could be understood with the char enhancement of phosphorus compounds through the proposed condensed-phase mechanism. Phosphorus and nitrogen in MPGE–DEP were conserved in the residue during the degradation process to form carbonaceous char. This phosphorus-containing char is extremely thermally stable and retards the weight loss of MPGE–DEP resin at high temperature region, as can be seen in Fig. 2. Moreover, it is noteworthy that nitrogen-containing compounds were observed only in the degradation products of MPGE–DDM, and not those of MPGE–DEP, indicating that these nitrogen-containing compounds might be only from the degradation of DDM structure. However, the evolution of isocyanatobenzene from the degradation of MPGE–DDM possibly implies that the maleimide groups decomposed below 410 °C. This result was therefore a discrepancy with the above-mentioned results from FTIR. Another explanation is that isocyanatobenzene was still from the decomposition of the DDM structure, and the maleimide groups remain in the solid residue to contribute to the high char yield of the MPGE resins.

The preservation of nitrogen of the maleimide groups in the residual of the maleimide degradation also enhanced the thermal stability of the residual char, especially for the MPGE–DEP resin. Further reactions between nitrogen and phosphorus should take place during the resin decomposition. These results further indicated a phosphorus–nitrogen synergistic effect on enhancing char formation as well as on flame retardation.

Table 3
The chemicals in the gases evolved from the degradation of MPGE based resins










































Test sample	Retention Time (min.)	Suspected Compound Name	Structure
MPGE-DDM 250-350 °C	2.28	3-methylpentane	
	2.46	acetic acid	
	2.66	benzene	
	3.80	toluene	
	5.06	o-xylene	
	5.19	p-xylene	
	6.27	isocyanato benzene	
	6.44	aniline	
	6.58	phenol	
	8.29	5,7-dimethylundecane	
	8.60	benzenamine 2-ethyl	
	9.17	aniline, N-methyl	
	9.70	o-ethylaniline	
MPGE-DDM 350-450 °C	2.28	3-methylpentane	
	2.46	acetic acid	
	3.80	toluene	
	6.49	aniline	
	6.71	phenol	
	7.56	2-methylphenol	
	7.72	p-aminotoluene	
	8.47	2-ethylphenol	

Table 3 (continued)

Test Sample	Retention Time (min.)	Suspected Compound Name	Structure	
MPGE-DDM 350-450 °C	8.64	2-ethylaniline		
	8.78	4-ethylaniline		
MPGE-DEP 250-350 °C	2.09	2-methylpentane		
	2.17	3-methylpentane		
	2.26	hexane		
	2.46	methylcyclopentane		
	2.59	acetic acid		
	MPGE-DEP 350-450 °C	2.11	2-methylpentane	
		2.18	3-methylpentane	
2.28		hexane		
2.48		methylcyclopentane		
2.66		benzene		
3.80		toluene		
5.19		p-xylene		
6.57		phenol		
7.72		4-methylphenol		
8.77		4-ethylphenol		
9.32		2,3-dihydrobenzofuran		
10.93		1,2-ethanediyl ester-2-methyl-2-propa noic acid		
14.03		1,2,3,4-tetrahydro-2-phenylnaphthalene		

Novel flame retardants having excellent thermal stability and superior flame retardance might be obtained from combining the maleimide and phosphorus groups in one compound. This concept is now being applied in developing new flame retardants for polymeric materials.

4. Conclusions

The kinetics and mechanisms of the degradation reactions of two thermosetting resins, MPGE–DDM and MPGE–DEP, were studied with TGA, FTIR, and GC/MS. Incorporation of phosphorous groups into the resin networks altered their degradation mechanisms through acid-catalysed dehydration and formed highly thermally stable char. The degradation of the maleimide groups was not accompanied by release of nitrogen-containing compounds, indicating that nitrogen groups were preserved in the degraded residual. This action also enhanced the thermal stability of the residual char. These results further indicated a phosphorus–nitrogen synergistic effect on enhancing char formation as well as on flame retardation.

Acknowledgements

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