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The effect of silicon sources on the mechanism of phosphorus–silicon synergism of flame retardation of epoxy resins

Ying-Ling Liu*, Ching-I Chou

Department of Chemical Engineering, Chung Yuan Christian University, 200 Chung-Pei Road, Chungli, Taoyuan 32023, Taiwan

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Abstract

The effect of silicon source on the mechanism and efficiency of silicon–phosphorus synergism of flame retardation was studied. The studied systems composed of a phosphorus-containing epoxy resin and various types of silicon additives including nanoscale colloidal silica (CS), tetraethoxysilane (TEOS), and diglycidylether terminated polydimethylsiloxane (PDMS-DG). Thermal stability and degradation kinetics of cured epoxy resins, elemental analysis of degraded residues, and evolved gases analysis of degradation reactions were conducted with a thermogravimetric analyser, energy-dispersive X-ray spectrometry, and gas chromatography–mass spectrometry, respectively. Addition of silicon compounds showed significant effect on enhancing the thermal stability and char yields of the cured epoxy resins. During thermal degradation, TEOS and PDMS-DG exhibited silicon migration to sample surface and CS did not. Self-degradation of PDMS-DG resulted in a silicon loss for PDMS-DG-containing epoxy resin. From the results it was concluded that using TEOS as an additive for epoxy resins and formation of epoxy-silica hybrid structure through sol–gel reactions was a good approach for achieving phosphorus–silicon synergism in flame retardation.

Keywords: Silicon; Flame retardation; Synergism; Thermal analysis

1. Introduction

"Environment-friendly" is one of the most important concepts for polymeric materials used in electronics. Among the topics, halogen-free epoxy resins receive mass research [1–5]. Phosphorus-containing compounds are utilized to replace the conventional brominated compounds in epoxy formulations. Epoxy resins modified with other chemical groups, such as imides [6–8], melamines [9], silicones [10,11], and nano-fillers [12–14] also show significant improvements on flame retardance. Consideration of cost reduction and property maintenance, increasing the efficiency of flame retardants is attractive so as to lower the amount of flame retardants used in epoxy formulations. Enhancement of flame retardancy of epoxy resins has been achieved by incorporation of phosphorus and silicon into epoxy resins with bringing a P–Si synergistic effect of flame retardation [15–20].

Hsiue et al. [15] reported that curing a phosphorus-containing epoxy with an aminopropylpolydimethylsiloxane (PDMS) resulted in epoxy resins exhibiting a high limited oxygen index (LOI) value of 45, which was hardly achieved by solely using phosphorous compounds. The high flame retardance of this epoxy resin might be from the actions of phosphorus and silicon through the mechanisms of (1) phosphorous groups degrading at relatively low temperatures to enrich char formation, (2) degradation of PDMS segments forming thermally stable silica structure, and (3) migration of silica to char surface serving as a protection layer to

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* Corresponding author. Tel.: +886 3 2654130; fax: +886 3 2654199.

E-mail address: ylliu@cycu.edu.tw (Y.-L. Liu).

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prevent further degradation of char at high temperatures. Similar phosphorus–silicon synergism of flame retardation was also observed with epoxy-silica hybrid resins, in which nanoscale silica was formed from sol–gel reactions of tetraethoxysilane (TEOS) [16,19,20], and with epoxy resins containing phosphorous and organosilicon groups [17,18]. High LOI values were observed with these epoxy resins and could be understood with the above-mentioned mechanisms.

Recently, preformed nanoscale silica particles were used as additives for formation of polymer-silica nanocomposites. Kashiwagi et al. [21] reported PMMA-silica nanocomposites showed a reduced heat release rate and mass loss rate in cone calorimetry. Yang and Nelson [22] also prepared PMMA-silica nanocomposites from silica particles. However, improvement on LOI values was not observed with the nanocomposites. Similar results were also observed in our previous work [23], in which addition of preformed nanosilica did not improve the flame retardance of epoxy-silica nanocomposites. The phosphorus–silicon synergism of flame retardation seems to not function in the phosphorus-epoxy/silica nanocomposites. It was postulated that the size of silica particles (about 10–20 nm) were too large to migrate to the char surface [23].

This study further examined the above postulations of the synergistic mechanisms of silicon in flame retardation. Epoxy resins from curing diglycidylether of bisphenol-A with diethylphosphite (DEP) formed the resin matrix [4]. Introduction of silicon into the epoxy resins was performed with three different approaches: using polydimethylsiloxane-diglycidylether terminated (PDMS-DG) as a reactive additive, utilizing TEOS and sol–gel reactions to form epoxy-silica hybrids, and adding silica nanoparticles to form epoxy-silica nanocomposites. The degradation behaviours and evolved gases analysis were conducted with a thermogravimetric analyser (TGA) and a gas chromatography–mass spectrometry. Elemental analysis and element mapping on the degraded chars were performed with scanning electronic microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDX).

2. Experimental

2.1. Materials

Diglycidylether of bisphenol-A (BE188, epoxy equivalent weight = 188 g/mol, Chang Chun Plastic Co., Taiwan), diethylphosphite (DEP, Aldrich Co.), tetraethoxysilane (TEOS, Aldrich Co.), and polydimethylsiloxane-diglycidylether terminated (PDMS-DG, epoxy equivalent weight = 490 g/mol, Aldrich Co.) were used as received. Nanoscale silica particles (CS) were purchased from Nissan Chemical Co., Japan. The commercial product of MIBK-ST, in which 30–31 wt% of silica (particle size: 10–20 nm) was dispersed in methylisobutylketone (MIBK), was used.

2.2. Characterization

FTIR spectra were measured with a Perkin Elmer Spectrum One FTIR. Differential scanning calorimetric thermograms were recorded with a Thermal Analysis (TA) DSC-Q10 in a nitrogen gas flow of 40 mL/min. Thermogravimetric analysis (TGA) was performed by a TA TGA-2050 at a heating rate of 10 °C/min under nitrogen or air. The gas flow rate was 100 mL/min. Scanning electron micrographs were observed with a Hitachi S-3000N Hi-SEM. Energy-dispersive X-ray (EDX) measurements were conducted with a Horiba ES-320 Energy Dispersive X-Ray Micro Analyser. Elemental analysis of phosphorus was measured with a micro digestion apparatus with a spectrophotometer. Limited oxygen index (LOI) values were measured on a Standton Redcraft flame meter. The percentage in the O_2–N_2 mixture deemed sufficient to sustain the flame was taken as the LOI. Evolved gases analysis was performed by collecting the evolved gases from a TGA (Perkin–Elmer TGA 7, at a heating rate of 10 °C/min. with a helium gas 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 keeping isothermal at 250 °C till the analysis was completed.

2.3. Preparation of cured epoxy resins

BE188, DEP, and silicon-containing additive were dissolved in tetrahydrofuran or methylethylketone to form a homogeneous solution. The amounts of BE188 and DEP were kept in stoichiometric ratios. Samples containing 5 and 10 wt% of silicon-containing additives were prepared. All of the solutions were evaporated at ambient condition for 24 h to remove the solvent. The residues were then thermally cured in an oven at 150 °C for 1 h, 180 °C for 1.5 h, and 220 °C for 3 h. The compositions for preparation of cured epoxy samples are tabulated in Table 1.

3. Results and discussion

3.1. Thermogravimetric analysis

The cured epoxy resins were first examined with a thermogravimetric analyser (TGA). Four parameters

Table 1
Preparation of cured epoxy resins containing phosphorus and silicon

Sample	Additive	Additive amount (wt%)	Phosphorus contents (wt%)
PER	–	–	3.5
ERCS-5	CS	5	3.0
ERCS-10	CS	10	3.0
ERTEOS-5	TEOS	5	3.2
ERTEOS-10	TEOS	10	2.5
ERPDMS-5	PDMS-DG	5	2.5
ERPDMS-10	PDMS-DG	10	2.6

of degradation temperature (T_d, temperatures at 5 wt% weight loss), activation energy of degradation reaction (E_a), integral procedural decomposition temperature (IPDT) [24], and char residue (CR) obtained from TGA thermograms were employed to probe the thermal properties of the cured resins. Typical TGA thermograms are shown in Fig. 1, and the analytical data are tabulated in Table 2. While heating in nitrogen, all samples excepting ERPDMS-5 showed similar degradation patterns. A rapid weight loss was observed at around 350–380 °C. Then, the decomposed residue lost part of their weights at 450–500 °C. The amount of weight loss for ERPDMS-5 was somewhat larger than that for other samples. The large amount of weight loss of ERPDMS-5 might be from the degradation of the organic glycidyl moiety of PDMS-DG. Degradation of this organic part also resulted in the low char ratio of ERPDMS-5 at 850 °C. On the other hand, high char yields were observed with ERCS-5 and ERTEOS-5 implying that some thermally stable char should form in the degradation periods of these two samples. While heating in air, very different degradation patterns were observed with various samples. A third stage of weight loss, arising from oxidative-degradation of the residues, was observed for PER at temperatures above 600 °C. Incorporation of silicon into the epoxy resins diminished this stage of weight loss. This phenomenon was also observed in previous reports [15,16], and was postulated to reduce the amounts of evolved combustible gases during degradation. According to the condensed phase mechanism of flame retardation [25], reduced amounts of evolved combustible gases as well as high char yields indicate good flame retardance. Based on the above, good flame retardance was expected with ERCS-5 since it exhibited a high char yield of 21.2 wt%. However, no improvement of flame retardance was observed with ERCS-5, as ERCS-5 exhibited a LOI value of 30.0, which was similar to the LOI value of pristine PER resin (29.5). As in previous work, PMMA-silica [22] and epoxy-silica [23] nanocomposites made from silica nanoparticles also showed high char yields but unimproved flammability. The high char yield of ERCS-5 should come from the inorganic CS additive, which showed no weight loss under heating. On the other hand, excepting for ERPDMS, increasing the amounts of silicon additives from 5 to 10 wt% further enhanced

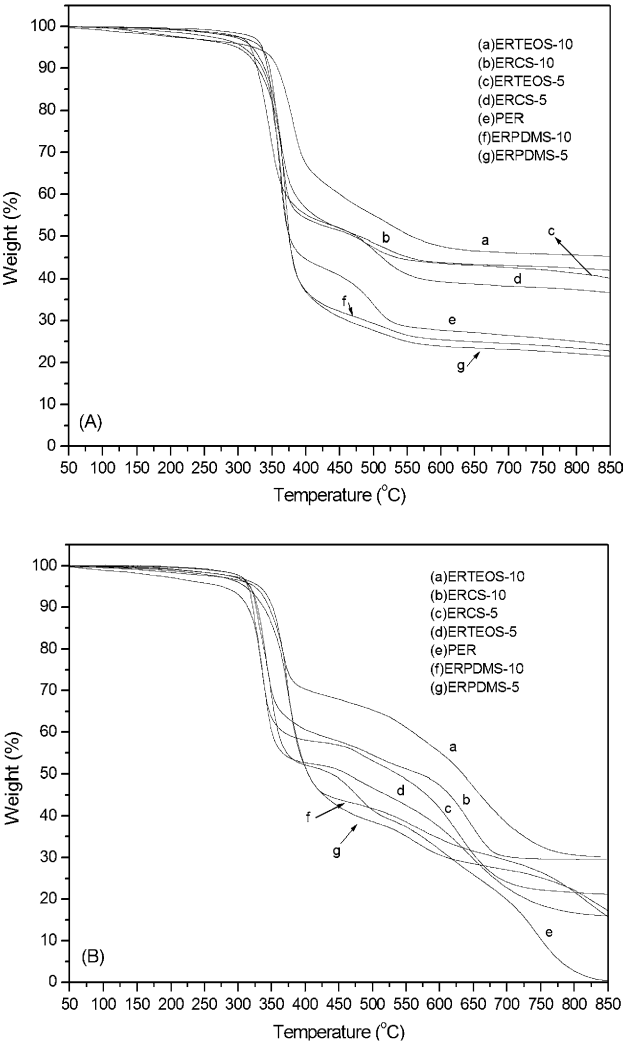


Fig. 1. TGA thermograms of PER and silicon-containing epoxy resins in (A) nitrogen and (B) air atmosphere.

Table 2
Thermal analysis data of epoxy resins containing phosphorus and silicon

Sample	Thermal degradation analysis data					
	In N_2			In air		
	T_d (°C)	Char yield[a] (wt%)	IPDT	T_d (°C)	Char yield[a] (wt%)	IPDT
PER	335	24.1	842	318	0.5	498
ERCS-5	319	36.6	1247	315	21.2	800
ERCS-10	334	42.0	1492	317	29.6	1004
ERTEOS-5	298	40.3	1403	277	16.0	688
ERTEOS-10	324	45.3	1637	324	30.2	1032
ERPDMS-5	307	21.5	768	311	17.2	713
ERPDMS-10	321	22.7	801	332	15.8	702

[a] Degraded residue weight at 850 °C.

char formation. The low char yield of ERPDMS-10 could be understood with degradation of the organic part of PDMS-DG. The high char yield (30.2 wt%) of ERTEOS-10 in air indicated that the degraded residue of this sample was extremely stable at high temperature in the presence of oxygen. Moreover, ERPDMS-10 showed a T_d of 332 °C (in air), which was much higher than that of ERPDMS-5 (310 °C). Similar result was observed with ERTEOS samples, but not for ERCS samples. The variance in T_d values of the samples implied that CS was not involved in the initial degradation reactions of ERCS resins, as mentioned above. The low T_d of ERTEOS-5 arose from the dehydration condensation reaction between silanol groups left from uncompleted gel reaction. Increase of the added TEOS amounts increased the conversion of gel reaction, so as to result in the high T_d of ERTEOS-10 [30,31]. The T_d values of ERPDMS in air were found to be higher than those in nitrogen. Oxidation of the resins might first form phosphorus/silicon-rich residues, which were relatively thermally stable and retard further degradation. Since T_d in this study was defined at the temperature of 5 wt% weight loss, the above-mentioned degradation retardation certainly shifted T_d to higher temperatures. Similar results were also observed with some other polymers containing char-forming elements and groups [32,33].

Activation energies of the degradation reactions were calculated from TGA data according to the method proposed by Ozawa [26]. Fig. 2 shows the activation energies of the degradation reactions at different conversions. Generally, incorporation of silicon into phosphorus-containing epoxy resins levelled their E_a values of degradation. For heating in air, ERTEOS-10 and ERPDMS-10 exhibited a dramatic increase of E_a values at degradation conversions above 40%. Referring to Fig. 1-B, the high E_a values indicated that some inhibition of thermal degradation occurred on ERTEOS-10 and ERPDMS-10 after their first stage of degradation in air. However, such effect was not observed with ERCS-10. The IPDT values of the samples calculated from TGA thermograms [24] are tabulated in Table 2. IPDT value was considered as an index of integral thermal stability and as an index of volatile parts of the tested materials. ERTEOS samples showed the most significant improvement on IPDT values, and ERPDMS samples showed lowest IPDT values. Incorporation of PDMS-DG increased the volatile parts of the cured resins to result in the low IPDT values of ERPDMS samples. The low IPDT values of ERPDMS samples in nitrogen might also imply that incorporation of PDMS-DG into the epoxy resins was not useful for increasing their thermal stability at high temperatures and for decreasing the amounts of evolved combustible gases. However, the test results in air showed a different result. First, the enhancing effect of silicon on thermo-oxidative stability of epoxy resins was demonstrated with the high IPDT values of the silicon-containing epoxy resins. In addition, the IPDT values of ERPDMS samples heated in air were similar to those in nitrogen, and other samples showed much lower values while heating in air. Therefore, PDMS-DG actually enhanced the oxidative stability of the epoxy resins.

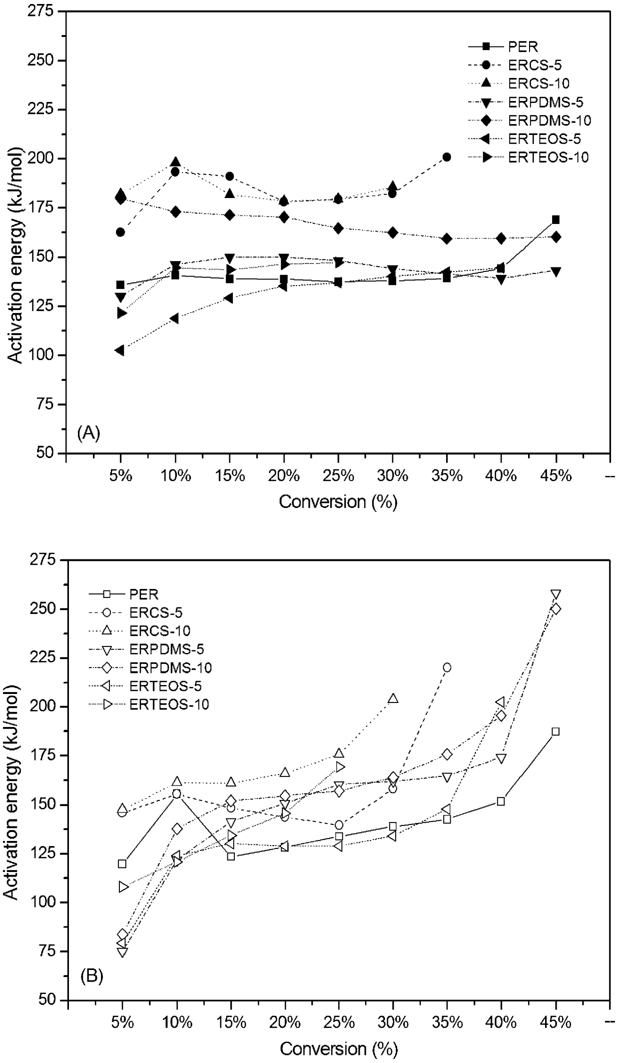


Fig. 2. Plots of activation energies of epoxy resin degradation vs. degradation conversions; (A) in nitrogen and (B) in air.

From the above discussion it was concluded that adding silicon compounds into phosphorus-containing epoxy resins raised their thermal stability and char yields. However, CS might not involve in the degradation reaction of epoxy resins, but PDMS-DG and TEOS did.

3.2. Elemental analysis with EDX

Char residues of the cured epoxy samples for elemental analysis were obtained from heating the

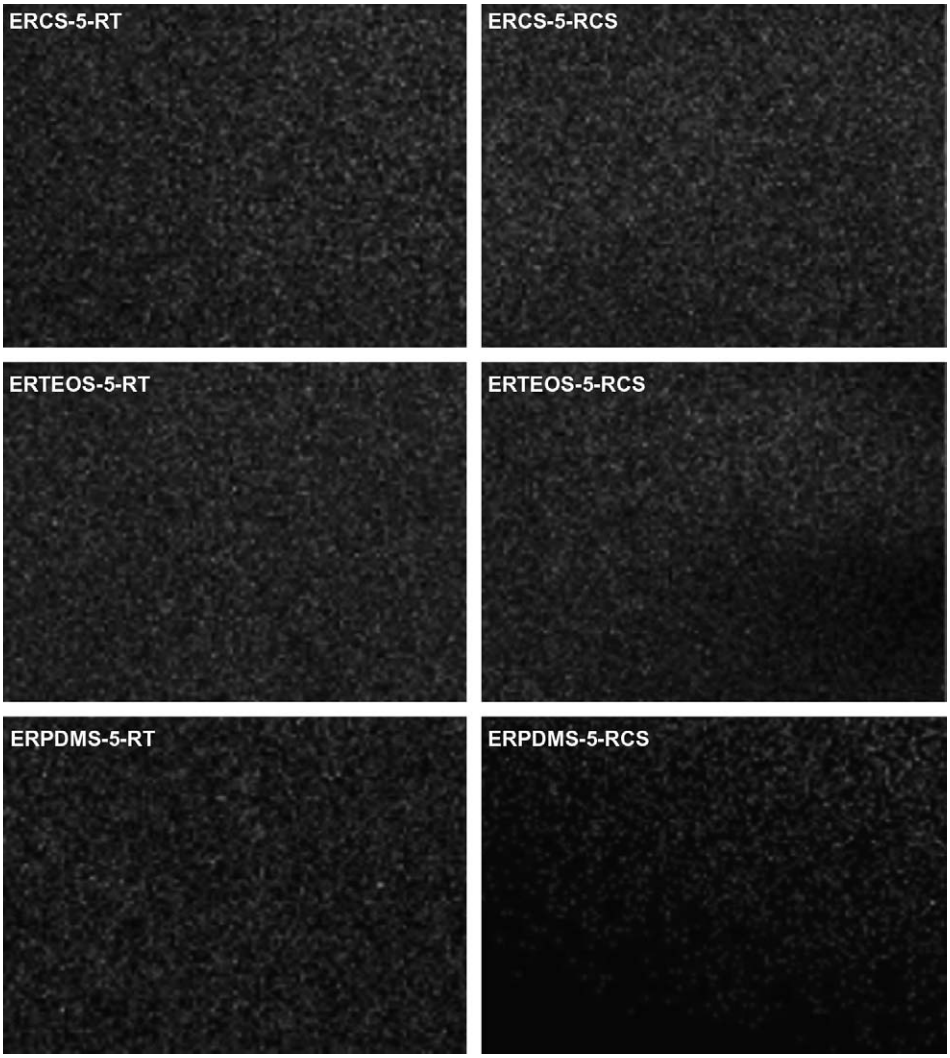


Fig. 3. SEM EDX Si-mapping micrographs of the degraded residues of the epoxy resins: (left) top surface, and (right) cross-sectional surface.

Table 3
Elemental analysis data of cured epoxy resins and their degraded residues

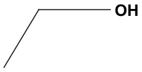
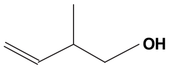
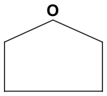
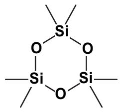
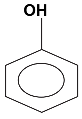
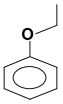
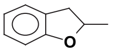
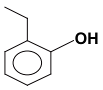
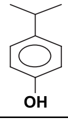
Sample[a]	Elemental analysis (mol%)			
	C	O	Si	P
PER	79.91	16.82	0.00	3.27
PER-RT	86.94	8.47	0.00	4.59
PER-RCS	87.33	7.74	0.00	4.92
ERCS-5	71.48	19.3	7.37	1.85
ERCS-5-RT	75.00	12.85	8.84	3.31
ERCS-5-RCS	53.70	29.6	13.32	3.38
ERTEOS-5	75.75	20.82	1.66	1.77
ERTEOS-RT	79.60	11.63	6.81	1.96
ERTEOS-RCS	74.29	17.75	6.05	1.91
ERPDMS-5	76.76	17.05	4.68	1.54
ERPDMS-5-RT	77.27	14.84	2.19	5.72
ERPDMS-5-RCS	74.35	17.01	2.77	5.87

[a] Cured resins were analysed with top-phase surface; -RT: top-phase surface of degraded residue; -RCS: cross-section of degraded residue.

samples under nitrogen from 30 to 900 °C with a heating rate of 10 °C/min. Elemental analysis and element mapping on the top-face (sample coded as -RT) and cross-section (sample coded as -RCS) surfaces of the char residues were performed with energy-dispersive X-ray spectroscopy (EDX). Silicon distributions in the cross-section phase of the degraded residues were directly observed with EDX element mapping, and the micrographs are shown in Fig. 3. The relatively low silicon density observed with the residue of ERPDMS-5 (ERPDMS-5R) indicated its low silicon content. Furthermore, ERCS-5R showed a homogeneous distribution of silicon in its cross-section phase, to indicate that silicon migration did not occur in the degradation process. On the other hand, silicon migration to surface was observed with both ERTEOS-5 and ERPDMS-5, as the silicon density increased with approaching the top surface.

Table 3 presents the elemental analysis results. The phosphorus content of PER char residue, compared with that of PER, increased from 3.3 to 4.6 mol%. An increase of P/C molar ratio from 4.1 to 5.3% was also observed. This result showed agreement with previous work which reported that phosphorus-rich char formed from thermal degradation of phosphorus-containing epoxy resins [27]. Similar results were also observed with other samples in this work. The elemental compositions of PER char residues obtained from top-face and cross-section surfaces were similar. However, obvious differences between the elemental compositions of top-face and cross-section surfaces were observed with the char residues of silicon-incorporated samples. First, the silicon content of ERTEOS-5 dramatically increased from 1.66 to 6.81 mol% after degradation. The high silicon content of ERTEOS-5 residue implied that most of the silicon remained in the condensed phase (char) after degradation. The silicon content of ERPDMS-5 residue was smaller than that of pristine ERPDMS-5, indicating some silicon loss to the gaseous phase during degradation. This loss of silicon was due to

Table 4
Degradation evolved gas of epoxy resins containing various silicon additives: 300–400 °C in nitrogen

Retention time in GC (min)	Structure	Peak area (%)			
		PER	ERCS-5	ERPDMS-5	ERTEOS-5
2.600 2.605		4.258	5.010	–	1.012
2.701 2.715		13.082	11.341	–	18.785
3.588		–	–	–	5.060
6.317		–	0.07	0.211	0.055
9.579 9.660 9.705 9.821		43.655	36.055	0.430	38.938
9.927 9.942 9.967		1.572	1.806	–	5.234
12.101 12.130		6.717	4.377	–	3.924
12.953		0.445	0.392	0.221	0.207
13.931 13.941 13.966	isomers 	6.348	9.188	4.852	1.980

the degradation of PDMS segments through formation of volatile cyclic products. In addition, comparing the silicon contents and Si/C molar ratios of the top-phase and cross-section surfaces of the residues, ERTEOS-5 showed a silicon-rich composition in top-face surface, to imply that silicon in ERTEOS-5 tended to migrate to the top-surface of the residue during thermal degradation. Meanwhile, ERPDMS-5 showed an almost homogeneous distribution of silicon in the residue. The relatively high silicon content of the cross-section surface of ERCS-5 residue indicated that most of the silicon is distributed in the bulk, rather than in the surface, of the ERCS-5 residue. The relatively high oxygen and low carbon contents in the cross-section of ERCS-5 residue further demonstrated that the residue contained certain amount of silica (SiO_2). This result might give a direct observation of that CS in ERCS-5 failed to migrate to top-phase surface during thermal degradation. For silica addition to thermoplastics, Kashiwagi et al. [28,29] reported that silica migration to polymer surface during thermal degradation was inhibited with the high melt viscosity of polymer. For the cases in this study, the epoxy resins were cross-linked and did not melt during heating. Therefore, silicon migration might be seriously inhibited with the network of epoxy resins. Moreover, surface area of silica additive also played an important role in migration [28,29]. The failure of CS migration during thermal degradation could be due to its high density and relatively small surface area and big volume, while comparing with silica formed from organo-silicon and controlled sol–gel reaction.

3.3. Evolved gas analysis with TGA–GC/MS

The evolved gases analysis on the epoxy samples were performed with a TGA–GC/MS. Degradation products obtained from the temperature region of 300 to 400 °C were collected and analysed (Table 4). PER and ERCS-5 showed almost same compositions of evolved gases, to indicate the added CS particles were not involved in the initial degradation reactions of the epoxy resin matrix. Cyclic dimethylsiloxane trimer (D3) was found in the degradation products for all of the test samples excepting PER, to reveal that some silicon elements might evolve out from the condensed phase to reduce the silicon contents of the residues. High content of D3 was observed with the evolved gas of ERPDMS-5 degradation. This gave direct evidence to that PDMS segment degraded under heat with formation of silicon-containing volatile products. As ethanol and 2-methyl-but-3ene-1-ol were not found in the evolved gases of ERPDMS-5 degradation, adding PDMS-DG into the epoxy resin inhibited the formation of highly combustible products in degradation. Moreover, the epoxy-silica hybrid structure in ERTEOS-5 was considered to serve as a barrier to confine the movements of the degradation products. The barrier effect was demonstrated with the reduced amount of ethanol and the appearance of some tetrahydrofuran in the evolved gas components of ERTEOS-5. The detained ethanol in the condensed phase then gained time for collision and reaction to form tetrahydrofuran.

4. Conclusion

Different silicon-containing additives in phosphorous epoxy resins showed various effect on resin degradation and synergistic effect of flame retardation. Nanoscale silica could not migrate to surface of degraded residues during thermal degradation of epoxy resin, and failed to show synergism with phosphorus on flame retardation. PDMS-DG and TEOS showed significant performance of silicon migration and could form a protective layer for preventing/retarding further degradation of char. Self-degradation of PDMS-DG during heating period resulted in some silicon loss in the condensed phase. Therefore, it was concluded that using TEOS as an additive for epoxy resins and formation of epoxy-silica hybrid structure through sol–gel reactions was a good approach for achieving phosphorus–silicon synergism of flame retardation in epoxy resins.

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