

Studies on the Thermal Properties and Flame Retardancy of Epoxy Resins Modified with Polysiloxane Containing Organophosphorus and Epoxide Groups

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ABSTRACT: A novel epoxy resin modifier, phosphorus-containing epoxide siloxane (PES) with pendant epoxide and cyclic phosphorus groups on the side chain of the polysiloxane backbone, was synthesized by the ring-opening reaction of epoxy-siloxane with 9, 10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO). PES was characterized by ¹H NMR and FT-IR measurements, and then it was employed to modify an epoxy resin at various ratios *via* pre-reaction with 4, 4'-diaminodiphenyl-methane (DDM) as curing agent. In order to compare with the epoxy resins modified with PES, DOPO-containing epoxy resins also cured under the same conditions. The thermal, thermomechanical, and flame-retardant properties of all cured polymers were investigated by differential scanning calorimetry (DSC), dynamic mechanical analysis (DMA), thermogravimetric analysis (TGA), the limited oxygen index (LOI) and cone calorimetry. The results showed that the epoxy resins modified with PES exhibited much better thermal properties and flame retardancy than the DOPO-containing epoxy resins at the same phosphorus content and the neat epoxy resin.
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KEY WORDS Epoxy / Siloxane / Phosphorus / Thermal Stability / Flame Retardancy /

In recent years, epoxy resins have been widely used in coatings, adhesives, aerospace and electronic industries, especially in microelectronic field. However, with the rapid development of electronic technology, the heat resistance and flame retardancy of conventional epoxy resins couldn't meet the requirements of these applications.^{1,2}

Much work has been done in an attempt to make epoxy resin more flame retardancy and great progress has been achieved so far.^{3–10} At present, with the consideration of avoiding the generation of toxic and halogenated gases, the trend is toward using environment-friendly flame retardant to modify the epoxy resins. One example is the use of organophosphorus, which shows evident effectiveness as a flame retardant.^{4–8} However, this increase in flame retardancy is always accompanied by a decrease in the initial decomposition temperature, which makes the modified epoxy resins unfit for those applications requiring critical thermal stability. Moreover, due to the limit from chemical structures in molecular design during the introduction of phosphorus, the low crosslink density of the cured epoxy resin often decreases T_g of the epoxy resin.^{9,10} According to a previous report,¹¹ the flame retardancy of phosphorus could be improved if providing an environment to reduce the thermal oxidation of phosphorus char at the high temperature region. Organosiloxanes possess many properties, including

hydrophobic property, non-flammability, excellent thermo-oxidative stability and electronic property, which can compensate for the disadvantages of phosphorus flame retardant. Thus, organosiloxanes would be one of choices for enhancing the flame retardancy and heat resistance.^{12–14}

In this paper, a novel modifier for epoxy resins, epoxy oligomer containing organophosphorus and organosilicon, was synthesized by the reaction of methylhydrosiloxane-dimethylsiloxane copolymer (MHS-DMS copolymer), allyl glycidyl ether (AGE) and DOPO. The structure of PES was confirmed by ¹H NMR and FT-IR measurements. PES at various ratios was exploited to modify the epoxy resin (Ep828) *via* pre-reaction of PES with DDM. Samples of the neat resin and the DOPO modified resins for comparison were also made. The thermal, thermomechanical, and flame-retardant properties of the cured products were characterized by DSC, DMA, TGA, LOI and cone calorimetry techniques.

EXPERIMENTAL

Materials

DOPO (Pwt % = 14.34) was obtained from TCI, DDM, triphenylphosphine (TPP) and hydrogen hexachloroplatinate hydrate (Pt-catalyst) were from Aldrich Chemical Co., AGE and MHS-DMS copoly-

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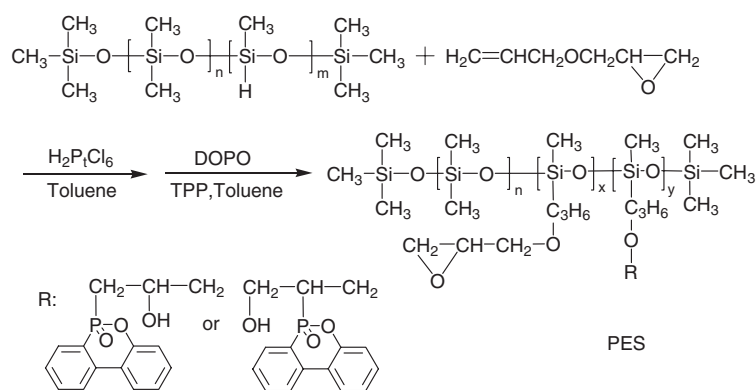


Figure 1. Synthesis of PES.

mer (reactive proton content was 1.41 wt %) were purchased from Xinghuo Chemical Co. of China, diglycidyl ether of bisphenol-A (Ep828, the epoxide equivalent weights (EEW) was 196 g/eq.) was from Shell Chemical Co., All solvents were reagent grade or were purified by standard methods.

Synthesis of the DOPO-Containing Epoxy-Siloxane

As shown in Figure 1, the synthesis of PES was a two-step reaction. The MHS-DMS copolymer, 50 g toluene and an excess of AGE (1.5 equivalents of Si-H) were first charged into a 250 mL four-necked flask with stirrer, thermometer, and reflux condenser. When the solution was heated to 75 °C, 1 wt % of Pt-catalyst was added to the flask under nitrogen and stirred until the end of reaction (the disappearance of absorption peak of the Si-H (2156 cm⁻¹) in the infrared spectra marked the completion of the reaction). Epoxy-siloxane (ES) was obtained by removing the excess AGE and the solvent using the rotary evaporator. Subsequently, ES, DOPO (0.5 equivalents of epoxide group), 0.2 wt % TPP (reaction promoter) and 60 g of toluene were orderly charged into a 250 mL four-necked flask. The mixture was allowed to reflux for 6 h and PES could be obtained by removing the solvent. Its EEW determined by the HClO₄/potentiometric titration method was 625 g/eq.¹⁵ FT-IR (cm⁻¹): 3430 (-OH), 3064 (C-H in phenyl group), 1587 (phenyl group), 1466 (P=Ph), 915 (epoxide ring). ¹H NMR (CDCl₃, ppm): 0.51 (4H), 1.59–1.61 (4H), 1.98–2.21 (1.8H), 2.58 (1H), 2.76 (1H), 3.12 (0.9H), 3.35–3.45, 3.65 (9.2H), 7.24–7.99 (8H).

Synthesis of the DOPO-Containing Epoxy Resin

The Ep828 was reacted with DOPO by opening epoxide groups (Figure 2). A typical example is shown below. 93.7 g Ep828 and 6.3 g DOPO (shown in Table I) were added into a four-necked flask equipped with stirrer, thermometer, and reflux condenser.

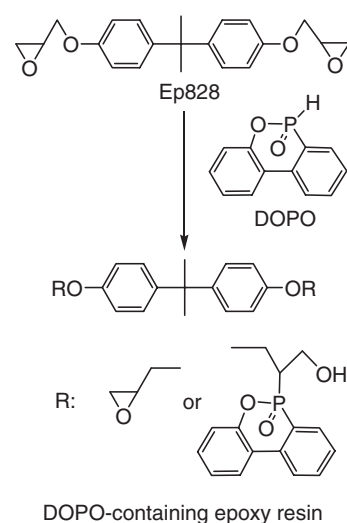


Figure 2. Preparation of DOPO-containing epoxy resin.

The reaction mixture was gradually heated to 160 °C and maintained at that temperature for 5 h. The DOPO-containing epoxy resin with the phosphorus content of 0.9 wt % was obtained. The epoxy resins of 0.3 wt % and 0.6 wt % phosphorus content were synthesized in the same manner.¹⁵

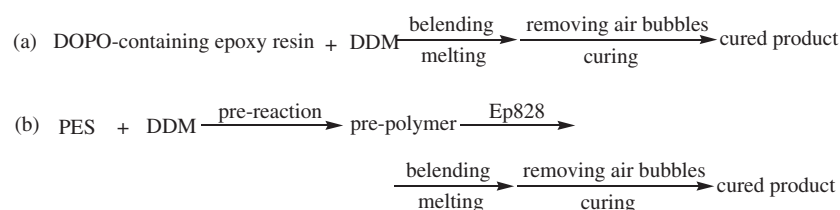
Curing Procedure of Epoxy Resins

100 mL xylene, designed amount of PES and calculated amount of DDM (according to the following equation, $m_{\text{DDM}} = M_{\text{DDM}} \times (n_1 + n_2) \times 1/4$, where m_{DDM} and M_{DDM} represent the mass and molecular weight of DDM, n_1 and n_2 are the molars of epoxide groups in PES and Ep828, respectively.) were first introduced into a four-neck round flask equipped with mechanical stirrer, thermometer, and reflux condenser. The mixture was allowed to react at 150 °C for 5 h. After that, the solution was then concentrated with a rotary evaporator and the pre-polymer was obtained. Ep828 (shown in Table I) and the corresponding pre-polymer were stirred and melt blended at 90 °C. A

Table I. Compositions of the prepared epoxy resins

Samples	Ep828/g	PES/g	DOPO/g	P Contents (wt %)	Si Contents (wt %)	DDM/g
Ep100	100	0	0	0	0	25.28
Ep98/DOPO2	97.9	0	2.1	0.3 ^a	0	24.26
Ep96/DOPO4	95.8	0	4.2	0.6 ^a	0	23.24
Ep94/DOPO6	93.7	0	6.3	0.9 ^a	0	22.23
Ep95/PES5	95	5	0	0.3 ^b	1.1	24.39
Ep90/PES10	90	10	0	0.6 ^b	2.3	23.51
Ep85/PES15	85	15	0	0.9 ^b	3.5	22.63

^aCalculated by the formula: (weight of DOPO/total weight of the system) $\times$ 14.34 wt % $\times$ 100%. ^bMeasured by the elemental analysis.

**Figure 3.** Schemes of curing procedure, (a) DOPO-containing epoxy resins, (b) Ep/PES epoxy resins.

vacuum oven was applied to remove air bubbles in the mixtures. Finally, the mixtures were poured into a mold to produce the samples. The curing conditions were 90 °C for 3 h, 150 °C for 2 h, and 175 °C for 1 h. After curing process was over, the cured products were demolded. As for the DOPO-containing and neat epoxy resins, the epoxy resin and equivalent DDM were blended at 90 °C and stirred until the mixture became homogenous. Samples of Ep100 and Ep/DOPO system cured under the same conditions as mentioned above. The amounts of materials used above were listed in Table I and the curing procedures were shown in Figure 3.

FT-IR, ¹H NMR and Elemental Analysis

Infrared spectrum (FT-IR) was recorded with RFX-65A FT-IR (Analect Co.). ¹H NMR was performed on a 400 MHz Brüker NMR spectrometer using CDCl₃ as solvent and tetramethylsilane as the internal reference. The phosphorus contents were determined *via* phosphorus elemental analysis by a micro-digestion apparatus with a spectrophotometer.

DSC

DSC measurements were performed on a Perkin-Elmer DSC-7 differential scanning calorimeter in a dry nitrogen atmosphere. The instrument was calibrated with standard indium. All samples were heated from 50 °C to 200 °C, and the thermograms were recorded at a heating rate of 10 °C/min. The glass transition temperature (*T*_g) was taken as the midpoint of the capacity change.

TGA

TGA was performed by a Perkin-Elmer thermogravimetric analyzer at a heating rate of 10 °C/min in both air and nitrogen atmosphere. The temperature ranged from 100 °C to 720 °C.

DMA

DMA was undertaken using a dynamic mechanical thermal analysis (DMTA) apparatus (TA DMA 2980). Specimens (2 mm $\times$ 10 mm $\times$ 30 mm) were tested in a three-point bend mold. The thermal transitions were studied in the 50 °C to 220 °C range at a heating rate of 5 °C/min and at a fixed frequency of 10 Hz.

Cone Calorimetry

Flammability was characterized by a cone calorimeter (standard type, Fire Testing Technology, UK) according to ASTM E 1354/ISO 5660. The sample sizes were 100 mm $\times$ 100 mm $\times$ 6 mm and the external heat flux level was 35 kW/m².

LOI

LOI values were measured on a ZRY-type instrument (China) with a test specimen bar of 120 mm $\times$ 6 mm $\times$ 3 mm according to the standard "oxygen index" test ASTM D-2863.

RESULTS AND DISCUSSION

Synthesis and Characterization of PES

Owing to the P-H group of DOPO showing high reactivity toward the oxirane group, the reaction has

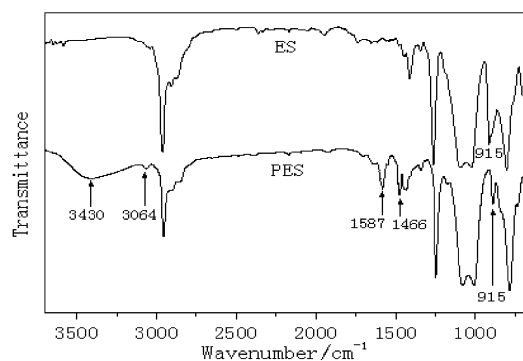


Figure 4. FT-IR spectra of PES and ES.

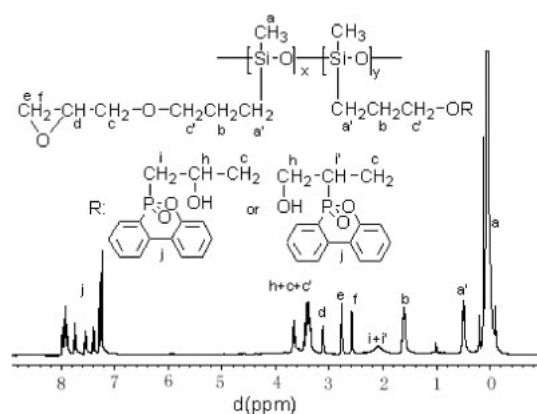


Figure 5. ^1H NMR spectrum of PES.

Table II. Thermal analysis data of the cured epoxy resins

Samples	T_g ($^{\circ}\text{C}$) by DSC	T_g ($^{\circ}\text{C}$) ^a by DMA	T_d 5% ($^{\circ}\text{C}$)		Char Yield at 720 $^{\circ}\text{C}$		LOI
			N_2	Air	N_2	Air	
Ep100	152.5	160.2	342.9	336.8	18.4	6.0	22
Ep98/DOPO2	147.4	155.8	337.6	334.1	18.7	8.3	22
Ep96/DOPO4	137.8	145.2	335.2	332.3	19.8	11.8	23
Ep94/DOPO6	126.5	135.6	330.4	329.5	22.0	15.1	24
Ep95/PES5	159.2	167.4	345.7	342.2	21.7	19.4	23
Ep90/PES10	166.4	177.7	354.0	353.1	23.9	22.3	25
Ep85/PES15	153.6	161.6	362.5	363.8	24.8	25.1	27

^aThe peak temperature of $\tan \delta$.

been widely applied to prepare DOPO derivatives.¹⁶ Through the reaction between P–H group and oxirane group, DOPO was incorporated into ES to synthesize PES, a kind of DOPO-containing epoxy-siloxane (Figure 1).

Seen from the FT-IR spectrums of PES and ES (Figure 4), no absorption peak at 2384 cm^{-1} (P–H) was observed in PES curve, and the appearance of the peak at 3430 cm^{-1} (–OH), which was an indication of the occurrence of the reaction. In addition, the appearance of the absorption peak at 1587 cm^{-1} (Ph), 3064 cm^{-1} (Ph–H) and 1466 cm^{-1} (P–Ph) indicated that the resulting PES contained the cyclic DOPO structure. The characteristic absorption peak at 915 cm^{-1} of the epoxide ring could be observed in this figure. As can be seen, the peak area in ES spectrum was about twice as large as that in PES spectrum, which indicated half of the oxirane groups in ES had undergone the reaction with DOPO.

The addition reaction between P–H and oxirane group might lead to the formation of two kinds of groups, *viz.*, –P–CH₂–CH(OH)– and HOCH₂CH(P)– groups by means of α and β addition of the epoxide ring. Both groups were observed easily from the ^1H NMR spectrum of PES. As shown in Figure 5, the peak at $\delta = 1.98\text{--}2.21\text{ ppm}$ (1.8H) was attributed

to the said two groups, which demonstrated the occurrence of the addition reaction of the P–H and epoxide ring. $\delta = 7.24\text{--}7.99\text{ ppm}$ (8H) belonged to the aromatic protons of the biphenol section and $\delta = 2.58\text{--}3.12\text{ ppm}$ (2.9H) were contained in the epoxide ring, which was an indication that equivalent epoxide groups and biphenyl groups existed in PES. Thus about half of all epoxide groups had been consumed in the reaction with DOPO, which was in good agreement with the results of FT-IR. Both FT-IR and ^1H NMR spectra of PES confirmed the chemical structure of the aimed product.

DSC Analysis of the Cured Epoxy Resins

T_g s of all cured products obtained by DSC were shown in Table II, it could be easily observed that the incorporation of only DOPO into Ep828 lowered its T_g apparently, the more DOPO the epoxy resin contained, the less stable it became. On the other hand, the epoxy resins modified with PES exhibited higher T_g s than that of Ep100 and epoxy resins only containing DOPO. For instance, the Ep90/PES10 had a maximal T_g of 166.4°C , which was about 14°C higher than that of Ep100, 28.6°C higher than the corresponding DOPO-modified epoxy resins. But this increase was followed by a decrease, as the con-

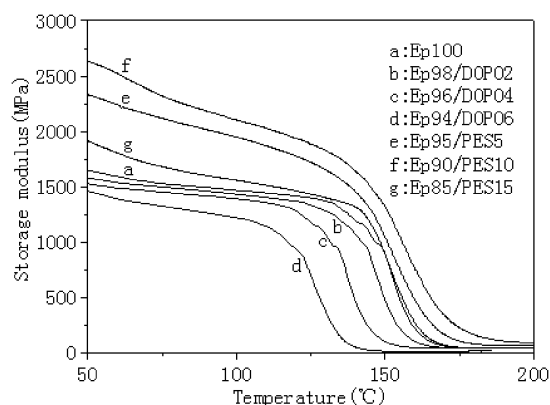


Figure 6. Storage modulus vs. temperature curves for the cured epoxy resins.

tent of PES became more than 10 wt %. The phenomenon could be explained by the following reasons: when PES at appropriate content was incorporated into Ep828 epoxy resins, it could react with DDM by its epoxide groups and entered into the crosslink network, which could function as the crosslink sites in some extent and led to higher crosslink density and consequently higher T_g . Another possible reason for the increase of T_g was that bulky rigid DOPO groups hindered the free movement of chains in Ep/PES system.^{5,6} When the content of PES exceeded certain value, despite chemically bonded into the network, the siloxane chains would not well dispersed in the continuous epoxy resin matrix due to the difference of their polarities, when PES served as a plasticizer and consequently resulted in the decrease in T_g owing to the plasticization effect of the soft siloxane chains. As for the DOPO-containing epoxy resins, owing to incorporating DOPO into Ep828 by opening oxirane groups, the crosslink density of Ep/DOPO system decreased largely, which effect to T_g greatly exceeded over the effect of the rigid DOPO structure and consequently Ep/DOPO system had lower T_g s than Ep100. Moreover, this decisive effect was more evident with the increase of DOPO, so the more DOPO the epoxy resin contained, the lower T_g it had.

Dynamic Mechanical Analysis

The dynamic mechanical behaviors of cured epoxy resins were obtained as a function of temperature from the glassy state to the rubbery plateau (Figure 6 and 7). The crosslink density of the cured product could be estimated from the plateau of the storage modulus in the rubbery state.¹⁷ In this paper, it was used to make qualitative comparisons of the level of crosslink among the various samples. As could be seen from Figure 6, the storage modulus of all the cured epoxy resins had similar change tendency with the increase of temperature, and the change of storage modulus

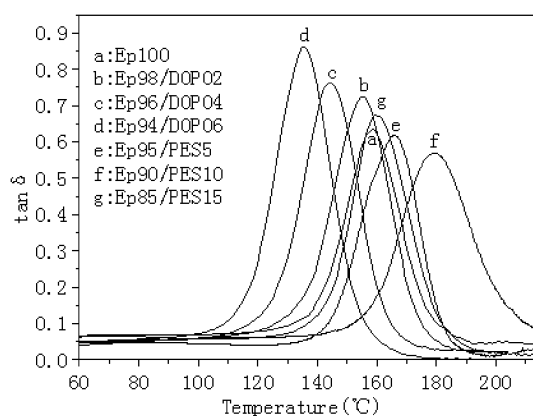


Figure 7. Tan δ vs. temperature curves for the cured epoxy resins.

at different P-content for all samples had the same trend as the T_g s by DSC analysis. The epoxy resins modified with 10 wt % PES exhibited the highest storage modulus, which indicated that it had the highest crosslink density in all the cured epoxy resins.

Figure 7 showed the $\tan \delta$ spectra of the cured epoxy resins. The temperature at which $\tan \delta$ reached its peak was generally thought to be T_g of the polymer. Clearly, increasing the phosphorus content in the Ep/DOPO system caused a substantial decrease of T_g , while the increase of PES in Ep/PES system led to an increase of T_g followed by a decrease. T_g s of the Ep/PES system were larger than that of the Ep100 and the Ep/DOPO system. For instance, T_g of Ep94/DOPO6 was 42.1 °C lower than that of Ep90/PES10. A lower value of the $\tan \delta$ was an indication of tighter crosslink network.¹⁷ Among all samples, Ep90/PES10 gave a comparatively small $\tan \delta$ value and small area under $\tan \delta$ curve, from which it can be inferred that Ep90/PES10 possessed high crosslink density. The high storage modulus and low $\tan \delta$ value of the Ep90/PES10 sample indicated its high cross-link density, which further affirmed that the explanation of its T_g obtained from DSC was right.

TGA Analysis of the Cured Epoxy Resins

TGA technique is another powerful means of evaluating the thermal stability of epoxy resins. TGA traces of the cured epoxy resins can provide important information about their thermal stability and thermal degradation behavior.¹⁸ TGA thermograms of the cured epoxy resins in air and nitrogen atmosphere were shown in Figures 8 and 9, respectively, and the details of the results were presented in Table II.

The initial degradation temperature, T_d 5%, was the temperature at which 5% weight loss of the tested sample was observed. It could be readily observed from Figures 8 and 9 that the addition of DOPO into Ep828 epoxy resin could lead to a reduction of their

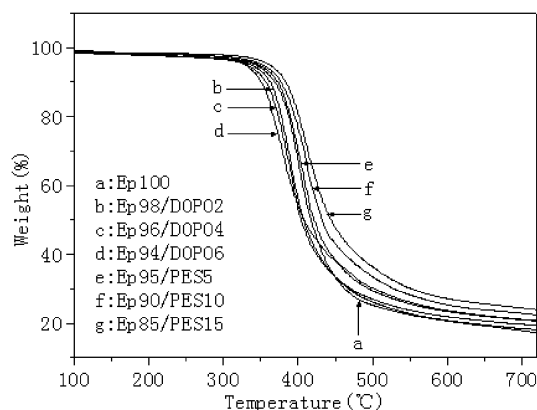


Figure 8. TGA curves of the cured epoxy resins in N_2 .

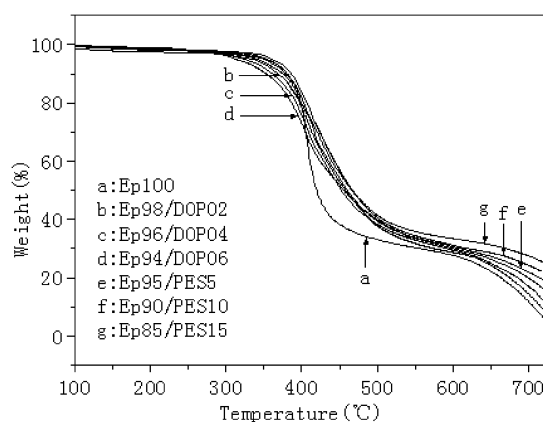


Figure 9. TGA curves of the cured epoxy resins in air.

T_d 5%. Conversely, T_d s 5% in Ep/PES system were much higher than that of the Ep100. For example, when the content of phosphorus was 0.3 wt %, the T_d 5% (345.7 °C) of Ep95/PES5 in N_2 was much higher than T_d 5% (337.6 °C) of Ep98/DOPO2.

The char yields of the epoxy resins were listed in Table II, it could be seen that the char yields increased as more phosphorus was incorporated into the epoxy resins, and a relatively larger char yields in the Ep/PES system could be observed, when comparing to Ep/DOPO system with the same phosphorus content. For instance, the char yield of the Ep95/PES5 was 21.7 in N_2 at 720 °C, while that of the Ep98/DOPO2 was only 18.7 at the same conditions. The existence of Si, which hardly vaporized even at elevated temperature, was rather critical for the higher char formation of Ep/PES system. It had been reported that high char yields implied high flame retardancy,²⁰ so the PES-modified epoxy resins showed better flame retardancy than the other epoxy resins.

From the discussions above, the PES-modified epoxy resins exhibited higher thermal stability and better flame retardancy and were superior to those of the mentioned phosphorus-containing epoxy resins.

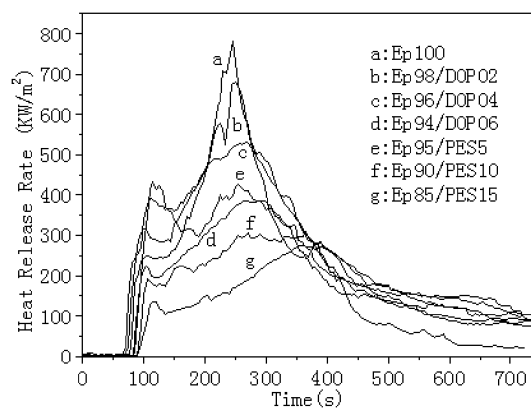


Figure 10. The HRR vs. time graphs for the cured epoxy resins.

In addition, it was interesting to note that the char-forming rate in air was different and slightly higher than that in N_2 when the content of PES was 15 wt %. One possible reason was that high-content epoxy-siloxane tended to form more silicon oxides in air, which resulted in a higher char-forming rate.

Flame Retardancy Analysis

The cone calorimeter is a very effective method for studying the flammability of materials. The results derived from the cone calorimeter turn out to be closely related to the large-scale results. The peak of heat release rate (PHRR) of a material is one of the most important factors to determine the potential behavior during fire.²¹ Figure 10 showed the change of heat release rate (HRR) of all the epoxy resins with time at a heat flux of 35 kW/m². The PHRR for Ep100 reached its peak after 250 s, with a value of around 781 kW/m², which was much higher than the modified epoxy resins. Ep94/DOPO6 had a PHRR of 384 kW/m², much lower than that of Ep100. With the same phosphorus content, Ep85/PES15 showed a PHRR of 271 kW/m², which was 65% lower than that of Ep100 and the lowest of all. Those indicated that silicon could improve the flame retardancy of the epoxy resins together with phosphorus.

Phosphorus and silicon are often used as flame-retardant elements, and they play critical roles in flame-retarding polymeric materials.¹⁶ The LOI can be used as an indicator to evaluate the flame retardancy of polymers. Therefore, the flame-retardant properties of these cured epoxy resins were further examined by measuring the LOI and the results were shown in Table II. With PES incorporated into the epoxy compositions, the LOI raised from 22 of Ep100 to 27 of Ep85/PES15, which was also higher than that of Ep94/DOPO6. The difference of LOI between Ep/PES and Ep/DOPO systems at the same phosphorus content might be attributed to the effect of silicon.

CONCLUSIONS

A novel modifier, DOPO-containing epoxide siloxane, was used to improve the thermal stability and flame retardancy of the epoxy resins. The chemical structure of PES was confirmed by FT-IR and ^1H NMR. DSC and DMA studies showed that the T_g s of Ep/PES system were higher than that of the other epoxy resins, especially than that of the epoxy resins modified only with DOPO. TGA, LOI and cone calorimetry measurements indicated that the Ep/PES system showed the highest flame retardancy of all mentioned epoxy resins. Unlike the epoxy resins modified only by DOPO, which exhibited lower thermal stability and better flame retardancy, the epoxy resins modified by PES showed better flame retardancy and thermal stability, which met the needs for more demanding applications.

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