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Novel phosphorus-containing epoxy resins
Part I. Synthesis and properties

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Abstract

Two series of novel multifunctional phosphorus-containing epoxy resins (phosphorus content 2 and 4%) were synthesized from the addition reaction of 9,10-dihydro-9-oxa-10-phosphaphenanthrene 10-oxide (DOPO) and the glycidyl ether of cresol formaldehyde novolac (functionality $= 12$, C_{12} and then cured with 4,4′-diaminodiphenyl sulfone (DDS), phenol novolac (PN) or dicyandiamide (DICY). The addition reaction was monitored by high performance liquid chromatography (HPLC) and epoxide equivalent weight (EEW) titration. The proposed structure was confirmed by FTIR and NMR spectra. Thermal properties of cured epoxy resins were studied using differential scanning calorimetry (DSC), dynamic mechanical analysis (DMA) and thermal gravimetric analysis (TGA). The flame-retardancy of cured epoxy resins was tested by UL-94 vertical test and limiting oxygen index (LOI). These cured epoxy resins exhibited high glass transition and high thermal stability and achieved UL-94 vertical tests of V-0 grade (nonflammable). © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Novel multifunctional epoxy resins; Cured epoxy resins; Flame-retardancy

1. Introduction

Advanced epoxy resins have been found to be particularly useful in the preparation of electrical and structural laminates, potting formulations, molding formulations and the like. These advanced epoxy resins are usually prepared by reacting an epoxy resin and an aromatic phenol in the presence of suitable advancement catalysts such as a phosphonium compound. Advanced epoxy resins containing bromine atoms are particularly useful for circuit boards application where flame-retardant property is desired. The resins in use are mainly the diglycidyl ether of bisphenol A (DGEBA) and the tetrabromobisphenol A (TBBA). The reaction is shown in Scheme 1. However, these bromine-containing advanced epoxy resins release hydrogen bromide, dibenzo-*p*-dioxin and dibenzo-furan during combustion, which cause corrosion and toxicity.

Furthermore, cresol epoxy novolac and TBBA epoxy are the resins typically employed to encapsulate microelectronic devices in molding compounds. The brominated resin, which is utilized as a flame-retardant additive to impart a degree of ignition resistance to the encapsulant contain many unstable hydrolyzable bromides, especially when they are annealed at high temperature, the hydrolyzable bromide increases dramatically [1,2]. These bromides, along with the presence of chloride impurities, are detrimental to the life of the electronic component. Specifically, bromine has been suspected and proven to cause wire bond failure [3].

Besides the halogen based compound, another method which can retard the combustion of polymer is blocking the source of fuel by covering the outer layer of the plastic with a nonflammable coating, such as alkyne-containing compounds [4–6] and phosphorus-containing compound [7–10]. Among these flame-retardant compounds, reactive organic phosphorus compounds give powerful flame-retardancy and thus attract more attention. Recently, some authors [7–10] have reported advanced epoxy resins containing phosphorus compound. One example [7] of the reaction is shown in Scheme 2.

Although these phosphorus-containing advancement epoxy resins exhibited good flame-retardancy, they exhibited low thermal stability. Furthermore, these advancement epoxy resins yield low glass transition and low crosslink density because they are derived from difunctional DGEBA and also due to their high EEW ($\mathrm{EEW} > 400$ g/eq). If advanced epoxy resins derived from multifuntional epoxy resins (functionality > 2) and phenolic compounds (diol or diacid), the advancement reaction may lead to gel

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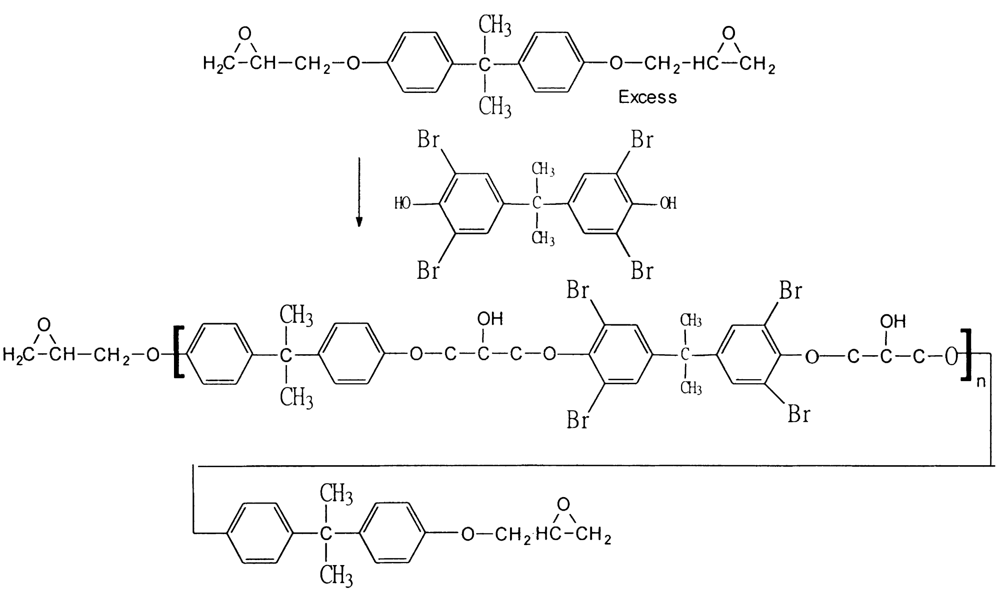


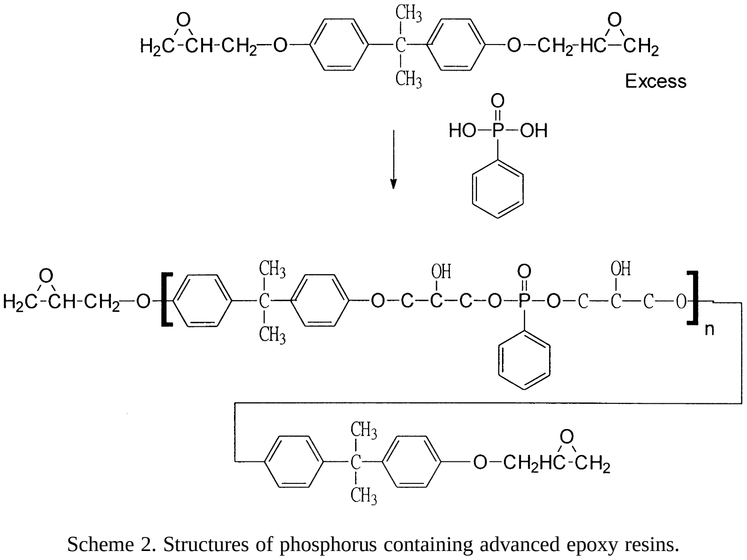
Scheme 1. Structures of bromine containing advanced epoxy resins.

if the reaction is not controlled well. In order to increase their T_g, multifunctional epoxy resin has to be added into these advanced resins. The blending of a multifunctional epoxy into these advanced resins may reduce their flame-retardancy as the multifunctional epoxy is not flame-retardant.

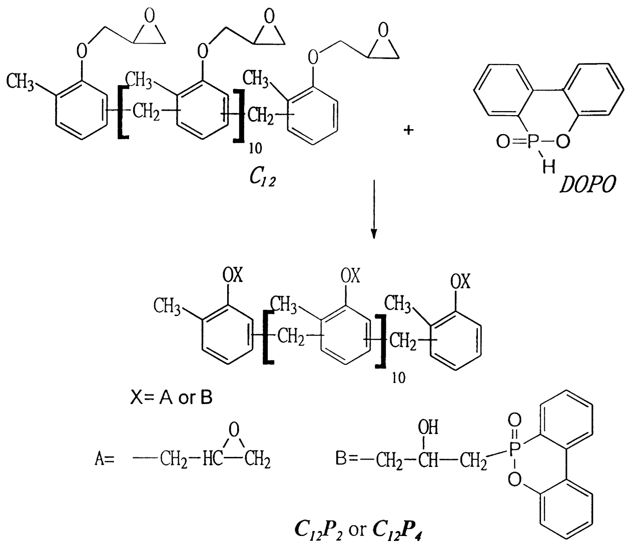
According to previous reports, DOPO with an active hydrogen can react with electron deficient compound, such as benzoquinoe [11,12] and maleic acid [13], which reminds us that DOPO might react at electron deficient carbon in oxirane ring. In this article, multifunctional phosphorus-containing epoxy resins for printed circuit board applications or epoxy molding compounds were synthesized by the addition reaction between DOPO and cresol formaldehyde novolac epoxy (functionality = 12, C_{12}). The reaction conditions were studied systematically by DSC, HPLC and EEW titration and the products were analyzed by ^{1}H- and ^{13}C NMR. The resulted epoxy resins were cured and their properties were evaluated by DSC, TGA, DMA, LOI and UL-94 vertical test and these data were compared with that of the neat cresol formaldehyde novolac epoxy system.

2. Materials

Cresol formaldehyde novolac epoxy resin (functionality = 12, C_{12}) with EEW 205 g/eq was supplied kindly by Nan Ya Plastics in People's Republic of China (trade name NPCN-704). PN with OH equivalent weight of 105 g/eq was supplied kindly by Chang Chun Petrochemical in People's Republic of China. Triphenyl phosphine (Ph_3P), DDS, and DICY were purchased from Acros. DOPO was



Scheme 2. Structures of phosphorus containing advanced epoxy resins.



Scheme 3. Structures multifunctional phosphorus containing epoxy resins.

purchased from TCI. All solvents used were commercial products (LC grade) and used without further purification.

3. Characterization

HPLC was employed with a Shimadzu LC-9A using a RP-18 column. DSC scans were obtained from samples of about 8 mg in a nitrogen atmosphere at a heating rate of 20°C/min using a Perkin–Elmer DSC 7. TGA was performed with a Perkin–Elmer TGA 7 at a heating rate of 20°C/min under nitrogen or air from 60 to 800°C. DMA was carried out with a Perkin–Elmer DMA 7e. The storage modulus G' and tan δ were determined as the sample was subjected to temperature scan mode at a programmed heating rate of 10°C/min from ambient to 300°C at a frequency of 1 Hz and an amplitude of 6 ℓm. A sample 15-mm in length, 10-mm in width and approximately 1.5-mm in thickness was used. The test method was performed by three point bending mode with a tension ratio at 110%. EEW of the epoxy resin and advanced epoxy resin were determined by the $HClO_4$/potentiometric titration method. The LOI was determined with an Atlas Limiting Oxygen Index Chamber according to the standard procedure (ASTM D-2863-77) with test specimen bar of 7–15 cm in length, 6.5 ± 0.5 mm in width and 3.0 ± 0.5 mm in thickness. The UL-94 vertical test was performed according to the testing procedure of FMVSS 302/ ZSO 3975 with test specimen bar of 127 mm in length, 12.7 mm in width and about 1.27 mm in thickness.

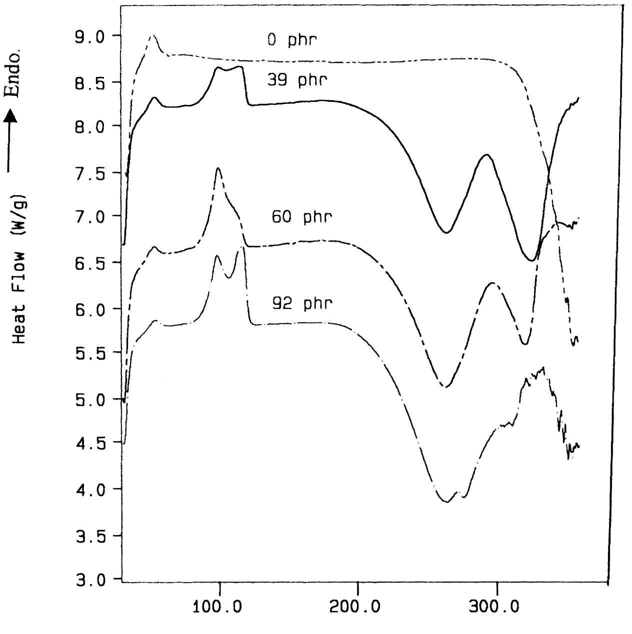


Fig. 1. DSC heating scans of 0, 39, 60 and 92 phr of DOPO in cresol formaldehyde novolac epoxy at a heating of 20°C/min.

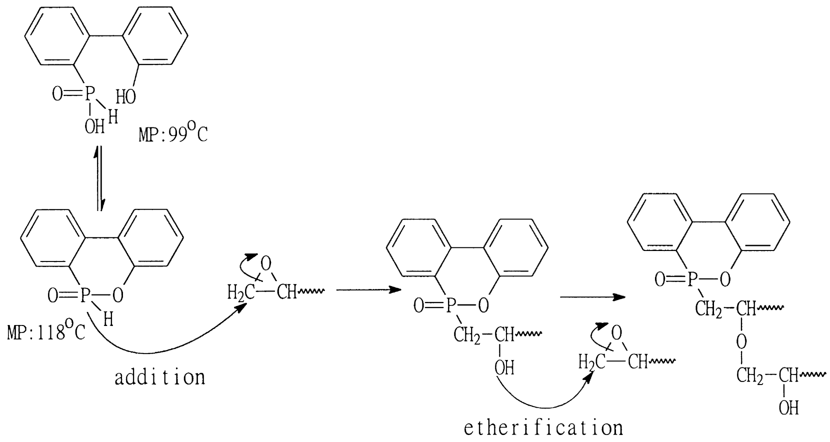
4. Synthesis of phosphorus containing epoxy resins

A typical example for $C_{12}P_2$ (phosphorus content is 2% wt/wt) is shown in Scheme 3. To a four-neck round-bottom flask equipped with a heating mantle, stirrer, thermocouple and temperature controller, C_{12} 400 g and DOPO 68 g were added. The reaction mixture was gradually heated to 160°C and maintained at that temperature for 150 min. Liquid chromatographic analysis of the reaction mixture has indicated a complete reaction of DOPO. A phosphorus containing epoxy with EEW 274 g/eq was obtained (285 g/eq theoretically).

$C_{12}P_4$ (phosphorus content is 4% wt/wt) was synthesized in the same manner as described above using DOPO 157 g. A phosphorus containing epoxy with EEW 485 g/eq was obtained (455 g/eq theoretically).

5. Curing procedure for advanced epoxy resins

C_{12}, $C_{12}P_2$ and $C_{12}P_4$ were separately cured with DDS, PN and DICY, respectively. The reactant compositions were mixed in a 1:1 equivalent ratio. The mixture was crushed into fine powder and then heated on a hot plate at about 150°C with continuous stirring until a homogeneous solution was obtained. DDS and DICY curing systems did not require a curing accelerator, but for PN curing system, 0.2 wt% of Ph_3P was added as an accelerator and stirred by hand until a homogeneous solution was obtained. The mixtures were cured at 160°C for 1 h, 180°C for 2 h, and 200°C for 2 h for $C_{12}P_2$ and $C_{12}P_4$ series. Another 220°C for 2 h was added to C_{12} series. After that, samples were allowed to cool slowly to room temperature in order to prevent cracking.



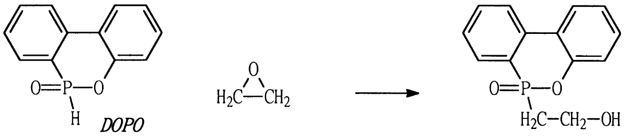
Scheme 4. The possible reaction occurred during DSC heating scan.

6. Result and discussion

6.1. Syntheses of $C_{12}P_2$ and $C_{12}P_4$

6.1.1. DSC analysis

DSC traces of neat C_{12} and 39,60 or 92 phr (parts per hundred of C_{12}) of DOPO in C_{12} (mixed well in a powder form) are shown in Fig. 1. According to the literature [13], DOPO is very hydrophilic and will react with moisture in air to form DOPO–H, thus the endothermic peak at 99°C is the melting of DOPO–H,and the other endothermic peak at about 118°C is the melting of DOPO. Since DOPO–H will dehydrate to form DOPO after melting [10], the undesirable byproduct (DOPO–H) in DOPO/C_{12} mixture will have no influence on the reaction between DOPO and epoxy group. Another exotherm started at about 160°C was observed and the exothermic peak increased with increasing phr of DOPO while no exotherm was observed below 280°C for neat C_{12}. Very recently, a Japanese patent [14] reported that DOPO reacted with ethylene oxide to form an addition product. The reaction is shown as follows:



Thus, the first exothermic peak may be attributed to the reaction between DOPO and oxirane ring in epoxy. Another exotherm started at about 290°C may be attributed to the etherification reaction of resulting aliphatic OH group and oxirane ring. The possible reactions discussed above are shown in Scheme 4.

6.1.2. HPLC trace and EEW titration

From DSC traces, one can find the reaction between DOPO and oxirane ring, but the completion of reaction time at certain reaction condition is unknown. Thus, LC traces and EEW titration was used to trace this reaction. LC traces show little reaction occurred between DOPO and C_{12} below120°C, even after 8 h at 120°C. When the reaction temperature was elevated to 160°C, the reaction occurred gradually and was completed in 150 min for $C_{12}P_2$ and $C_{12}P_4$. Another method to trace the reaction is by EEW titration. For the $C_{12}P_2$ system, EEW at zero conversion is total weight/moles of epoxy ring at zero conversion $= (400 + 68)/(400/205) = 240$ g/eq and EEW

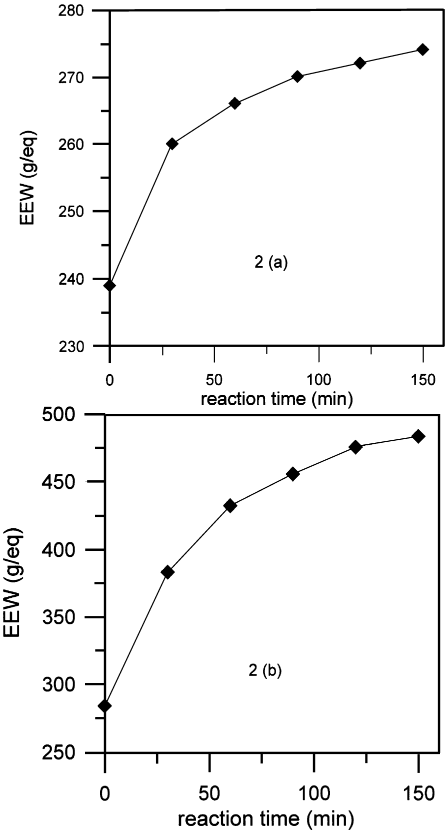


Fig. 2. The relation between EEW and reaction time for: (a) $C_{12}P_2$ and (b) $C_{12}P_4$ system.

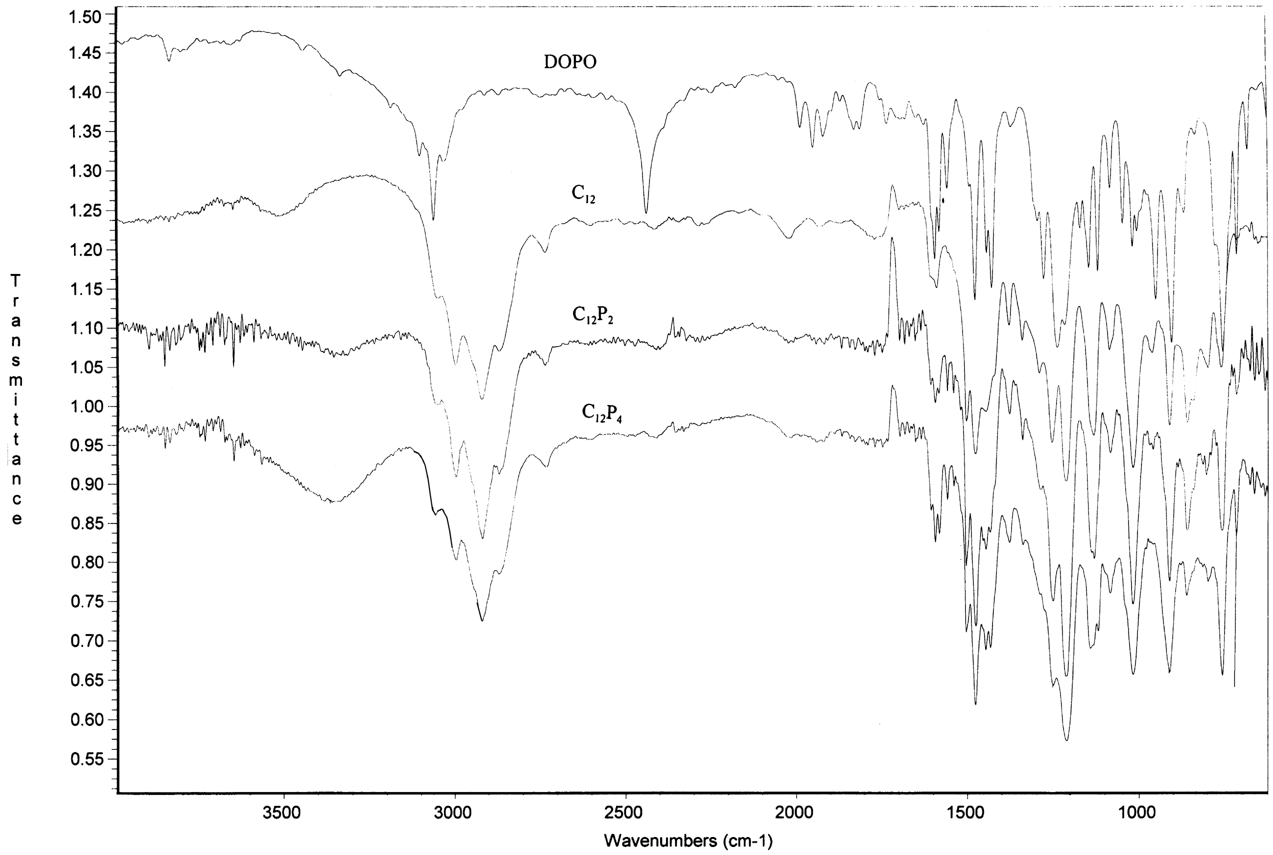


Fig. 3. IR spectra of DOPO, C_{12}, $C_{12}P_2$ and $C_{12}P_4$.

at 100% conversion is total weight/moles of epoxy ring at 100% conversion = (400 + 68)/(400/205 − 68/216) = 286 g/eq, theoretically. Fig. 2(a) shows the relation between EEW and reaction time. EEW increases with time and reaches a constant value after 150 min implying the reaction is near completion after 150 min, which is consistent with HPLC trace. For the $C_{12}P_4$ system, EEW at zero conversion is total weight/moles of epoxy ring at zero conversion = (400 + 157)/(400/205) = 285 g/eq and EEW at 100% conversion is total weight/moles of epoxy ring at 100% conversion = (400 + 157)/(400/205 − 157/216) = 455 g/eq, theoretically. Fig. 2(b) also shows EEW increases with time and reaches a constant value after at 150 min implying the reaction is completed after 150 min, which is also consistent with HPLC trace. However, higher EEW (485 g/eq) than theoretical value (455 g/eq) was detected in the $C_{12}P_4$ system, which may be attributed to the etherification reaction in this system. The etherification reaction may be caused by inhomogeneity in reaction temperature and high viscosity of the reaction mixture. However, the etherification reaction is not observed in the $C_{12}P_2$ system because the mixture is not as viscous as the $C_{12}P_4$ system and thus the reaction temperature has been well controlled. According to HPLC traces and EEW titration, DOPO–C_{12} adducts were synthesized at 160°C for 150 min for both $C_{12}P_2$ and $C_{12}P_4$.

6.1.3. Characterization of uncured epoxy resins

Fig. 3 shows the IR spectra of DOPO, C_{12}, $C_{12}P_2$ and $C_{12}P_4$. A strong P–H absorption at 2400 cm^{-1} was observed for DOPO and an OH absorption at around 3500 cm^{-1} is observed for C_{12}, which is due to the advancement reaction of C_{12} during manufacturing process. For $C_{12}P_2$ and $C_{12}P_4$ system, there is another OH absorption at around 3360 cm^{-1}, which is consistent with the proposed structure shown in Scheme 3. Fig. 4(a) and (b) show ^1H NMR and ^{13}C NMR spectra of $C_{12}P_4$, respectively. The assignments shown in Fig. 4(a) and (b) were obtained by $^1H–^1H$ HMQC, $^1H–^1H$ HMBC, $^1H–^{13}C$ HETERCOR and DEPT 135 (not shown here for brief) and the spectra confirmed the proposed structure.

6.2. Thermal properties of cured epoxy resins

6.2.1. TGA analysis

TGA traces of cured epoxy provided additional information regarding their thermal stability and thermal degradation behavior. TGA curves of C_{12}/DDS, $C_{12}P_2$/DDS and $C_{12}P_4$/DDS under nitrogen and air were shown in Table 1. The onset degradation (T_d onset) temperatures decrease with phosphorus content, however, char yields increase with phosphorus content. Generally speaking, the reduction of T_d may be attributed to the decrease of crosslink density

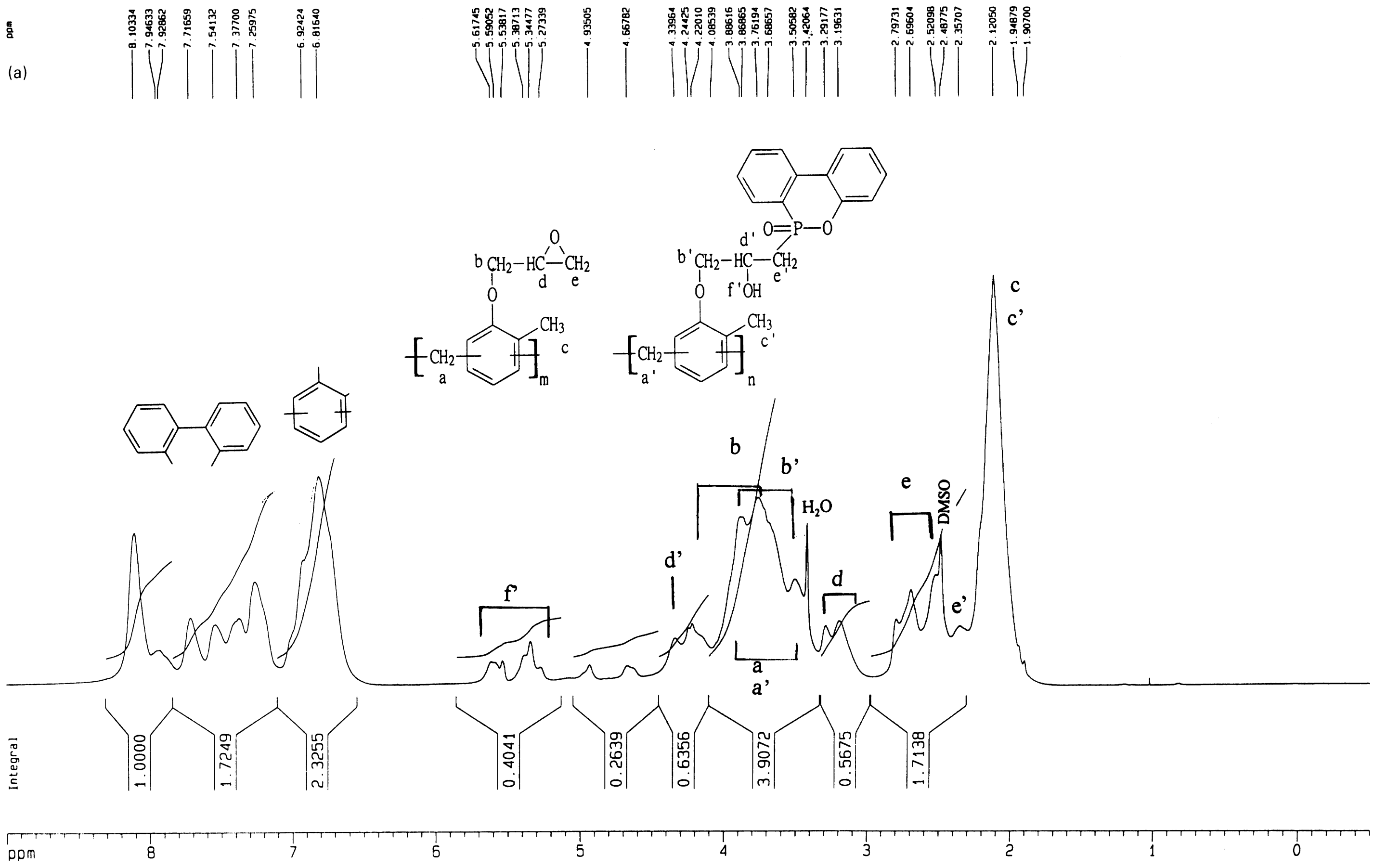


Fig. 4. (a) ^{1}H NMR and (b) ^{13}C NMR of $C_{12}P_4$.

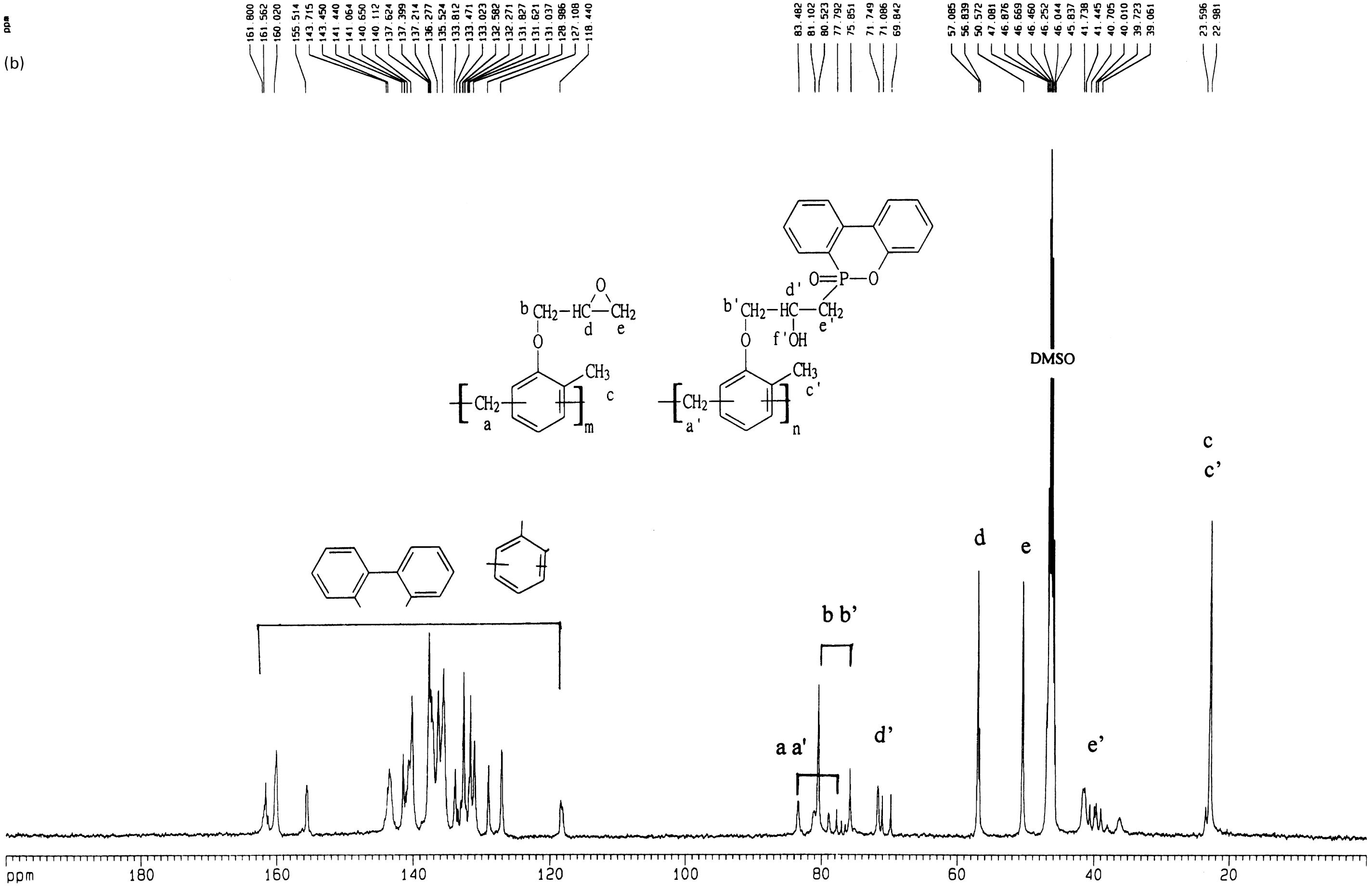


Fig. 4. (*continued*)

Table 1
TGA analysis of cured epoxy resins

Sample ID	T_d 5%°C		Char yield at 700°C	
	N_2	Air	N_2	Air
C_{12}/DDS	407	416	29.9	0
$C_{12}P_2$/DDS	386	387	42.3	25
$C_{12}P_4$/DDS	371	374	43.6	29.5
C_{12}/PN	407	408	40.1	0
$C_{12}P_2$/PN	391	394	47.6	35
$C_{12}P_4$/PN	376	378	46.7	41
C_{12}/DICY	373	380	29.3	2.2
$C_{12}P_2$/DICY	363	370	33.7	21.4
$C_{12}P_4$/DICY	364	370	35.0	27.9

of phosphorus containing epoxy resins and the O=P–O is less stable than common –C–C– bond. However, comparing with other phosphorus containing polymers [15,16], the decomposition temperatures of these phosphorus containing epoxies were extremely high. Yokoyama et al. [17–23] have reported that polymers with a high aromatic content would possess both fire retardancy as well as thermal stability. The high T_d in the resulted epoxy may be attributed to the high aromatic content of DOPO. "It may also be attributed to the cyclic O=P–O chain being more thermally stable than open one [15,16,22,23], that is, an introduction of doubly stranded units into the backbone has exhibited better thermal stability than the open one" [17–21]. TGA traces of the cured advanced epoxy resins showed higher char yields than that of C_{12}/DDS under nitrogen and air. Less than 1% char yield was found in C_{12}/DDS at 700°C under air, however, 25 and 30% char yields were found in $C_{12}P_2$/DDS and $C_{12}P_4$/DDS systems, respectively. Van Krevelen [24] has proposed that the char residue on pyrolysis is linearly proportional to the oxygen index of halogen-free polymers. Increasing the char formation will limit the production of combustible gases, decrease the exothermicity of the pyrolysis reaction, and decrease the thermal conductivity of the burning materials, and consequently limit the flammability of the materials. The results shown in Table 1 indicate that the flame-retardancy of $C_{12}P_2$ and $C_{12}P_4$ were elevated via the phosphorus group. Furthermore, the residual char increases with phosphorus content indicating the flame-retardancy was increased with phosphorus content. This is consistent with LOI and UL-94 measurement discussed below. Similar TGA results were observed in other systems (curing agent: PN or DICY) and the results are shown in Table 1. From Table 1, we can find 5% decomposition temperature (T_{d5}) in air is higher than that in nitrogen. This behavior may be attributed to the decomposition of the phosphorus group at earlier stages in air, forming a protection layer on the polymer surface, which raised T_{d5} of these cured epoxy resins.

6.2.2. DMA analysis

More detailed information may be obtained from measurements of the dynamic mechanical behavior of the samples as a function of temperature. Fig. 5 showed the dynamic mechanical analyses of C_{12}/DDS, $C_{12}P_2$/DDS and $C_{12}P_4$/DDS at a heating rate of 10°C/min from 0 to 300°C. Their T_gs are 255, 228 and 178°C, respectively. The heights of loss tangent are 0.163, 0.221, 0.482, respectively. The storage moduli at 50°C are 10.2, 10.6, 10.5×10^8 Pa; and at $T_g + 40$°C are 1.06, 0.31, and 0.09×10^8 Pa, respectively. The modulus at 50°C is not a function of phosphorus content indicating the incorporation of DOPO into epoxy would not reduce the rigidity of the resulted epoxies. This may be attributed to the high rigidity of DOPO, which compensates somewhat of the loss in crosslink density. However, at high temperature, modulus is $C_{12}/DDS > C_{12}P_2/DDS > C_{12}P_4/DDS$ and height of loss tangent is $C_{12}/DDS < C_{12}P_2/DDS < C_{12}P_4/DDS$ indicating the incorporation of DOPO into epoxy will reduce its crosslink density and rigidity at high temperature. According to rubber elasticity theory [25]: the crosslink density is proportionate to the storage modulus at $T_g + 40$°C, thus the ratio of crosslink density for C_{12}/DDS: $C_{12}P_2$/DDS: $C_{12}P_4$/DDS is 11.7:3.4:1. Similar TGA results were observed in other systems (curing agent: PN or DICY) and the results are shown in Table 2. Although incorporating DOPO into epoxy resins will reduce their T_g and crosslink density, their T_gs are still higher than other phosphorus containing advanced epoxy resins for FR-4 application.

6.2.3. LOI and UL-94 measurement

The LOI value can be used as an indicator to evaluate

Table 2
DMA analysis of cured epoxy resins

Sample ID	T_g°C (DMA)	Height of loss tangent	Modulus 50°C (10^8 Pa)	Modulus $T_g + 40$°C (10^8 Pa)
C_{12}/DDS	255	0.163	10.2	1.06
$C_{12}P_2$/DDS	228	0.221	10.6	0.31
$C_{12}P_4$/DDS	178	0.482	10.5	0.09
C_{12}/PN	216	0.132	21.2	0.75
$C_{12}P_2$/PN	178	0.423	28.9	0.32
$C_{12}P_4$/PN	155	0.747	23.7	0.11
C_{12}/DICY	248	0.053	12.3	1.28
$C_{12}P_2$/DICY	213	0.200	17.8	0.5
$C_{12}P_4$/DICY	169	0.465	12.5	0.15

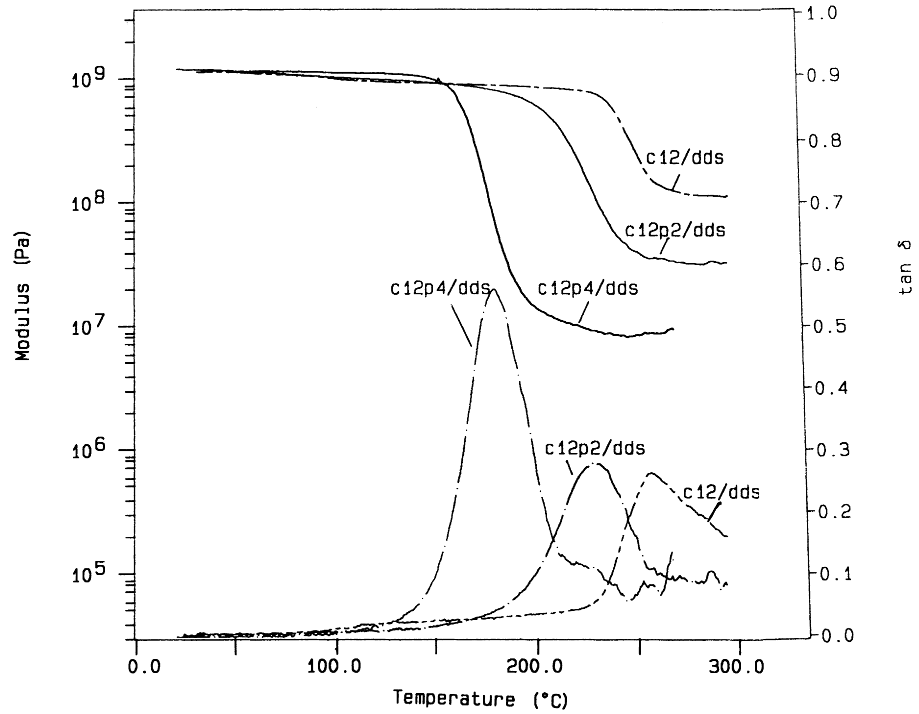


Fig. 5. DMA traces of C_{12}/DDS, $C_{12}P_2$/DDS and $C_{12}P_4$/DDS.

flame-retardancy of polymers. LOI is defined as the minimum fraction of oxygen in an oxygen–nitrogen mixture that is just sufficient to sustain combustion of the specimen after ignition. Thus, the flame-retardant properties of these cured epoxy resins were further examined by measuring the LOI and the results are shown in Table 3. Table 3 demonstrates that a higher LOI value is obtained with higher phosphorus content. It increases drastically from 23 to 27 when phosphorus content was increased from 0 to 1.69% and increases to 33 when phosphorus content was 3.63%. A material with LOI of 26 or higher is rated as a flame-retardant material, thus incorporating 1.69% of phosphorus into epoxy chain will make these epoxies as flame-retardant polymers. Other LOI values are listed in Table 3. LOI of $C_{12}P_2$/DICY is 34, which is higher than $C_{12}P_2$/DDS and $C_{12}P_2$/PN. This may be attributed to the nitrogen content in DICY (N = 67%) is higher than DDS (N = 11.2%) and PN (N = 0%). Nitrogen–phosphorus synergistic effect may account for the results. The other reason is the low hydrogen equivalence of DICY, which results in high phosphorus content for the cured epoxy. Thus, the flame-retardancy is DICY system > DDS system > PN system.

Table 3
UL-94 test and LOI measurement of cured epoxy resins

Sample ID	P%	VL-94 Grade	LOI
C_{12}/DDS	0	V-2	23
$C_{12}P_2$/DDS	1.69	V-0	27
$C_{12}P_4$/DDS	3.63	V-0	33
C_{12}/PN	0	V-2	21
$C_{12}P_2$/PN	1.45	V-0	26
$C_{12}P_4$/PN	3.29	V-0	28
C_{12}/DICY	0	V-2	24
$C_{12}P_2$/DICY	1.86	V-0	34
$C_{12}P_4$/DICY	3.83	V-0	38

UL-94 is another testing method for flame-retardancy. During the test, the polymer specimen was subjected to two 10-s ignitions. After the first ignition, the flame was removed and the time for the polymer to self-extinguish (t_1) was recorded. Cotton ignition would be noted if polymer dripping occurred during test. After cooling, the second ignition was performed on the same sample and the self-extinguishing time (t_2) and dripping characteristics were recorded. If $t_1 + t_2$ is less than 10 s with no dripping, it is considered to be a V–0 material, an industrial standard for flame-retardancy. As shown in Table 3, the UL-94 rating increases from V-2 grade for C_{12} series to V–0 for $C_{12}P_2$ and $C_{12}P_4$ series, which is consistent with the results of LOI measurements. Although $C_{12}P_2$ system and $C_{12}P_4$ system all exhibited V–0 grade, the flame-retardancy increased with phosphorus content. ($C_{12}P_2$/DICY, $t_1 + t_2 < 5$ s; $C_{12}P_4$/DICY, $t_1 + t_2 < 2$ s).

7. Conclusion

Novel phosphorus-containing epoxy resins were synthesized from the addition reaction of DOPO and cresol formaldehyde novolac epoxy. The reaction was monitored by HPLC and the structure was confirmed by FTIR and NMR spectra. The flame-retardancy of cured epoxy resins was examined by LOI measurement and UL-94 vertical test, and found to be excellent. TGA measurements show cured epoxy resins have high thermal stability compared with other phosphorus-containing polymers. DMA measurements show the cured epoxy resins exhibit good modulus and high glass transition temperature. For example: if phosphorus content of uncured epoxy resins is 2% (meet the criterion of flame-retardancy), $T_g = 228°C$ for DDS curing system; $T_g = 178°C$ for PN curing system and $T_g = 213°C$ for DICY curing system. Furthermore, these multifunctional phosphorus-containing epoxy resins are soluble in acetone and other common solvents, which is an advantage for printed circuit laminates industry. These properties should make this epoxy attractive for practical applications such as halogen-free flame-retardant laminates and epoxy molding compounds with high glass transition temperature.

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