

Synthesis and Properties of Flame-Retardant Epoxy Resins Based on DOPO and One of Its Analog DPPO

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ABSTRACT: Two phosphorus-containing heterocyclic flame retardants -9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO) and 2,8-dimethyl-phenoxaphosphin-10-oxide (DPPO) - and their derivatives were characterized and incorporated in the backbone of epoxy novolac to obtain flame-retardant epoxy resins. The structures and spectroscopic data including high-resolution mass spectroscopy of these flame retardants were determined. Flame-retardant epoxy resins with a phosphorus content of up to 2% based on heterocyclic DOPO and DPPO were cured with 4,4'-diaminodiphenylmethane (DDM), and their features were examined by UL 94, LOI, and DSC. In this manner, high-performance polymers with glass transition

temperatures around 190°C and the UL 94 rating V0 were obtained. These polymers were compared with epoxy resins incorporating diphenyl phosphite and diphenyl phosphate, which are nonheterocyclic and do not pass the UL 94 test up to 2% phosphorus. DPPO has a similar flame retardancy like the commercially available DOPO. Furthermore, to explain the difference in the efficiency of the tested flame retardants, key experiments for the determination of the active species during the flame-retarding process were performed and the PO radical was identified © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 105: 685–696, 2007

Key words: flame retardance; resins; crystal structures

INTRODUCTION

Epoxy resins have excellent characteristics of moisture, solvent, and chemical resistance, toughness, low shrinkage on cure, superior electrical and mechanical resistance properties, and good adhesion to many substrates.^{1–4} However, flammability of such resins is a major disadvantage in applications that require high flame resistance. Many techniques were applied to improve their flame retardancy. Recently, phosphorus-modified epoxy resins have received most attention in literature. This approach involves the synthesis of epoxy resins and hardeners from monomers bearing phosphorus groups that are effective as a flame retardant or thermal stabilizer.^{1–4}

Various organic phosphorus groups were covalently incorporated in the backbone of epoxy resins to improve their flame retardancy.^{5,6} Since a heterocyclic organic phosphorus compound, 9,10-dihydro-9-

oxa-10-phosphaphenanthrene-10-oxide (DOPO), was developed in the early 1970's, a large number of applications and modifications of this flame retardant have been published.^{3–11} These systems are commercially applied for printed circuit boards and laminates.

The aim of this article is the introduction and assessment of a novel phosphorus containing heterocycle as a flame retardant, and its comparison to its analog DOPO and two nonheterocyclic compounds. The effectiveness of these heterocyclic compounds is to be demonstrated.

This study describes the synthesis (Fig. 1) and characterization of the DOPO analog compound 2,8-dimethyl-phenoxaphosphin-10-oxide (DPPO), its modifications, and incorporation in an epoxy novolac (Fig. 2).

Furthermore, the same modifications and incorporations were made with DOPO (Fig. 3) and compared to its analog and to diphenyl phosphite and diphenyl phosphate (Fig. 4). The mode of action of phosphorus-containing flame retardants is discussed based on high-resolution mass spectroscopy and thermal desorption mass spectroscopy. The PO radical was detected exclusively as a small volatile phosphorus-containing species in the case of heterocyclic flame retardants.

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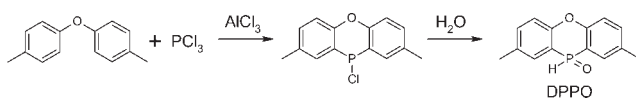


Figure 1 The systematic synthesis route of DPPO.

EXPERIMENTAL

Materials and reagents

Aqueous formaldehyde solution (37%), aqueous hydrogen peroxide solution (30%), ethanol, phosphorus trichloride, aluminum trichloride, diphenyl phosphite, diphenyl phosphate, and 4,4'-diaminodiphenylmethane (DDM) were purchased from Aldrich and used without any further purification. Triethanolamine, benzene, and toluene were obtained from VWR. Epoxy Novolac (DEN 438) was used from DOW AG and DOPO was kindly donated by Schill und Seilacher AG.

Measurement and testing

^1H and ^{31}P NMR spectra were obtained by a Bruker Analytical BZH 250/52 Spectrometer at 250 MHz. Samples were analyzed in deuterated DMSO or CDCl_3 .

Differential scanning calorimeter (DSC) measurements were done using a Mettler - Toledo DSC 822 $^\circ$ at a scan rate of 20 $^\circ\text{C}/\text{min}$.¹² The measurements were performed in aluminum pots with weighted samples of 20 mg.

The UL 94 vertical burning classification was obtained using an ATLAS HVUL 2 burning chamber according to DIN IEC 60,695-11-10 with a 50 W burner flame. The sample were (130 \pm 1) mm long, (13 \pm 1) mm wide and had a thickness of (7 \pm 1) mm.¹³

The LOI was obtained with a FTT LOI burning chamber according to ISO 4589-2.¹⁴

X-ray analysis was performed using a Siemens SMART CCD 1000 diffractometer with an irradiation time of 10–20 s per frame, thus collecting a full

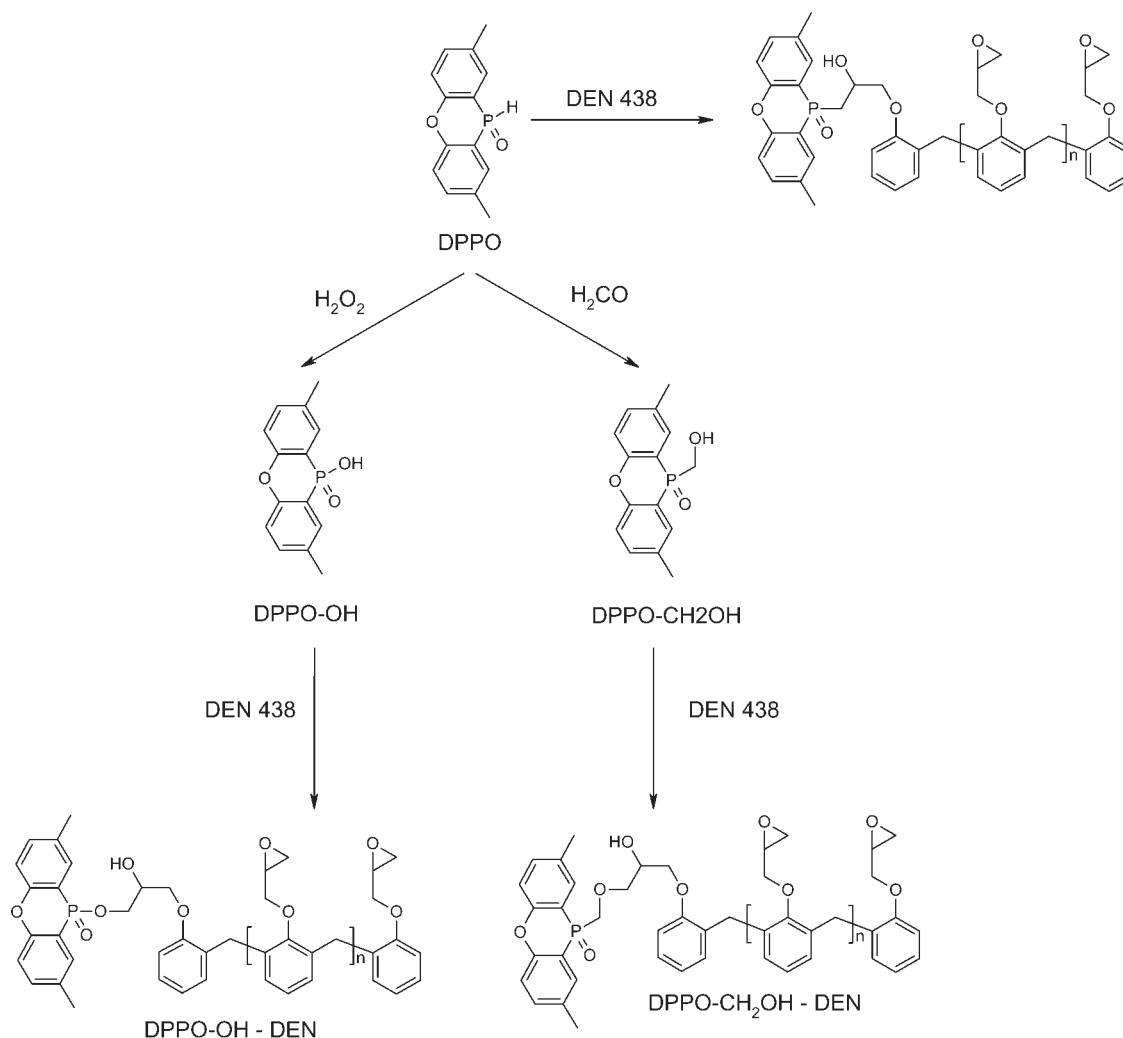


Figure 2 The systematic synthesis routes of flame-retardant epoxy resins based on DPPO ($n = 3.6$).

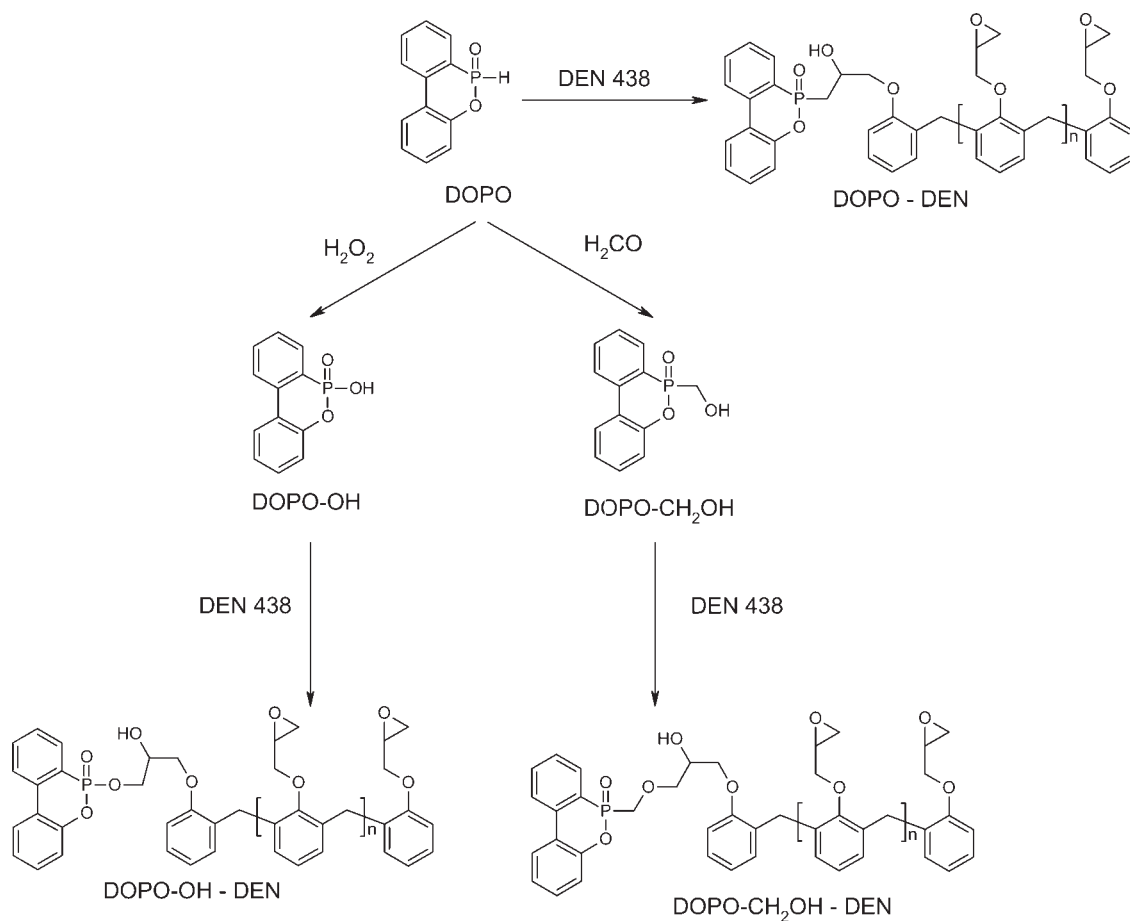


Figure 3 The systematic synthesis routes of flame-retardant epoxy resins based on DOPO ($n = 3.6$).

sphere of data using an ω -scan technique with $\Delta\omega$ ranging from 0.3° to 0.45° . Experimental absorption correction was performed with SADABS.¹⁵

Single crystals of DOPO and DPPO were obtained by recrystallization out of toluene and benzene, respectively.

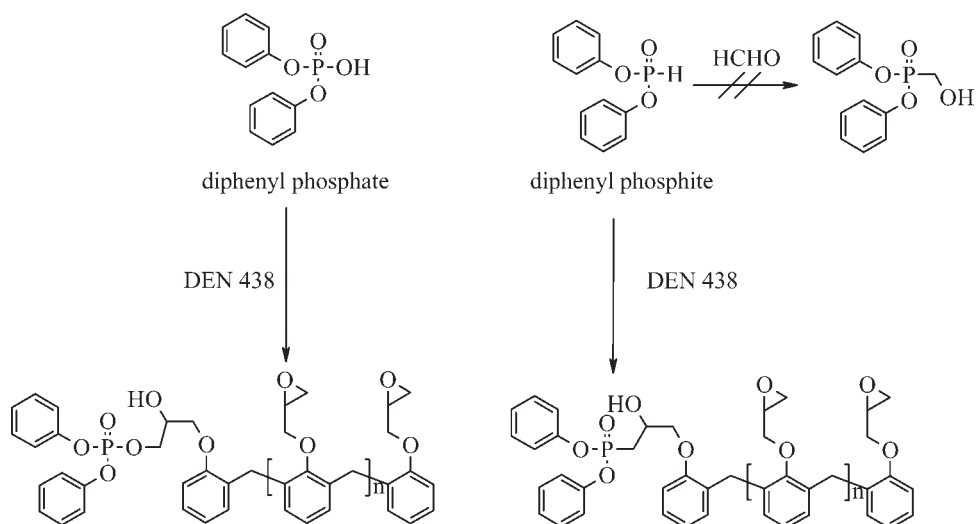


Figure 4 The systematic synthesis routes of flame-retardant epoxy resins based on diphenyl phosphite and its oxidized form (diphenyl phosphate) ($n = 3.6$).

Crystallographic data of the structures were deposited at the Cambridge crystallographic database centre (CCDC), supplementary publications Nos. 617870 (DPPO) and 617871 (DOPO). Structure solution and refinement were performed with SHELX 97.¹⁶

Copies of this information may be obtained free of charge from: The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336033, e-mail: deposit@ccdc.cam.ac.uk).

High-resolution mass spectrometry was carried out using a time-of-flight GCT from Micromass.

Thermal desorption mass spectroscopy was performed in vacuum chamber coupled to a heatable sample-carrier out of stainless steel, a high-vacuum system from Pfeiffer and a HAL IV RGA 201 from HIDEN Analyticals, UK. Powdered samples of the cured resins (10–20 mg) were charged to the sample carrier and the system was evacuated (10^{-8} hPa). The cured resins were heated from room temperature to 460°C at a heating rate of 10°C/min and the pyrolysis gases were detected with the mass spectrometer. The way from the sample carrier to the detector was about 50 cm. The signals were correlated with the also measured mass of 11 amu, to correct the influence of the pressure increase during the pyrolysis.

DPPO synthesis

The methods suggested^{17,18} were modified as follows:

59.40 g (0.30 mol) bis-*p*-tolylether, 105 mL phosphorus trichloride, and 39.6 g aluminum trichloride were fed into a 1 L three-necked round bottom flask equipped with a stirrer and a condenser with exhaust pipe. The reaction mixture was heated carefully to 85°C with stirring for 24 h. During this period, an intense gas formation (HCl) was observed and a white precipitate was formed. The reaction mixture was cooled down and poured onto 1 kg crushed ice. The product was filtered, thoroughly washed with hydrochloride acid solution (1.0 mol/L), saturated sodium bicarbonate solution, and finally with distilled water. The white powder was recrystallized from benzene and dried under vacuum (15 hPa) at 120°C for 24 h. The yield of DPPO was 91%.

¹H-NMR (CDCl₃): 2.406 ppm (s, 6H); 7.196 ppm (m, 2H); 7.409 ppm (m, 2H); 7.763 ppm (d, 2H); 8.550 ppm (d, 1 P—H).

³¹P-NMR (CDCl₃): -16.486 ppm (s).

HRMS: found: 244.0623 u; calc.: 244.0653 u.

Synthesis of DPPO-CH₂OH

DPPO, 61.02 g (0.25 mol), and 300 mL ethanol were charged to a 1 L three-necked round bottom flask equipped with a stirrer, a condenser and an addition funnel. The reaction mixture was heated to 70°C with stirring, where as 22.3 g of a 37% aqueous

formaldehyde solution were added in a dropwise manner over a period of 30 min. After the complete addition of the aqueous formaldehyde solution, the reaction mixture was maintained at about 80°C for an additional 12 h. The reaction mixture was concentrated by distillation, resulting in the precipitation of the product. The latter was filtered, thoroughly washed with ethanol, and dried under vacuum (15 hPa) at 120°C for 24 h. The yield of DPPO—CH₂OH was 82%.

¹H-NMR (DMSO-d₆): 2.381 ppm (s, 6H); 3.373 ppm (s, 1H); 4.050 ppm (s, 2H); 7.265 ppm (m, 2H); 7.498 ppm (m, 2H); 7.711 ppm (m, 2H).

³¹P-NMR (DMSO-d₆): 7.643 ppm (s).

HRMS found: 274.0735 u; calc.: 274.0759 u.

Synthesis of DPPO-OH^{19,17}

DPPO, 61.02 g (0.25 mol), and 300 mL ethanol were filled into a 1 L three-necked round bottom flask equipped with a stirrer, a condenser, and an addition funnel. The reaction mixture was heated to 70°C under stirring, where as 250 mL of a 30% aqueous hydrogen peroxide solution were added drop wise over a period of 30 min. During the addition, an intense gas formation was observed. After the complete addition of the aqueous hydrogen peroxide solution, the reaction mixture was maintained at about 80°C for an additional 12 h. The reaction mixture volume was reduced by distillation, resulting in the precipitation of the product. The product was filtered, washed thoroughly with ethanol, and dried under vacuum (15 hPa) at 120°C for 24 h. The yield of DPPO—OH was 77%.

¹H-NMR (DMSO-d₆): 2.37 ppm (s, 6H); 7.232 ppm (m, 2H); 7.442 ppm (m, 2H); 7.569 ppm (t, 2H).

³¹P-NMR (DMSO-d₆): 2.320 ppm (s).

HRMS: found: 260.0616 u; calc.: 260.0602 u.

Synthesis of DOPO-CH₂OH^{20–23}

The method suggested by Shieh and Wang²³ was modified as follows:

DOPO, 216.17 g (1.0 mol), and 650 mL ethanol were fed into a 1 L three-necked round bottom flask equipped with a stirrer, a condenser, and an addition funnel. The reaction mixture was heated to 70°C under stirring, where as 89 g of a 37% aqueous formaldehyde solution were added in a dropwise manner over a period of 30 min. After this, the reaction mixture was maintained at about 80°C for an additional 6 h, resulting in the precipitation of the product. The latter was filtered, washed thoroughly with ethanol, and dried under vacuum (15 hPa) at 120°C for 24 h. The yield of DOPO—CH₂OH was 86%; melting point 154°C.

TABLE I
Overview of the Actual Compositions of the Synthesized Flame-Retardant Epoxy Resins
Based on DOPO and its Derivatives

Number	DEN (g)	DOPO (g)	DOPO-OH (g)	DOPO-CH ₂ OH (g)	Catalyst (g)	Phosphorus content (% P)	Flame retardant content (%)
1-1	100.00	3.61			0.1	0.50	3.5
1-2	100.00	5.51			0.1	0.75	5.2
1-3	100.00	7.49			0.1	1.00	7.0
1-4	100.00	9.54			0.1	1.25	8.7
1-5	100.00	11.67			0.1	1.50	10.5
1-6	100.00	16.19			0.1	2.00	13.9
2-1	100.00		3.89		0.1	0.50	3.7
2-2	100.00		5.95		0.1	0.75	5.6
2-3	100.00		8.09		0.1	1.00	7.5
2-4	100.00		10.32		0.1	1.25	9.3
2-5	100.00		12.65		0.1	1.50	11.2
2-6	100.00		17.60		0.1	2.00	15.0
3-1	100.00			4.13	0.1	0.50	4.0
3-2	100.00			6.33	0.1	0.75	5.9
3-3	100.00			8.62	0.1	1.00	7.9
3-4	100.00			11.01	0.1	1.25	9.9
3-5	100.00			13.51	0.1	1.50	11.9
3-6	100.00			18.87	0.1	2.00	15.9

¹H-NMR (DMSO-d₆): 4.26 ppm (m, 2H); 5.56 ppm (t, 1H); 7.26 ppm (m, 2H); 7.45 ppm (t, 1H); 7.62 ppm (t, 1H); 7.78 ppm (m, 1H); 8.05 ppm (t, 1H); 8.19 ppm (m, 2H).

³¹P-NMR (DMSO-d₆): 32.8 ppm (s).

HRMS: found: 246.0461 u; calc.: 246.0446 u.

Synthesis of DOPO-OH²⁴⁻²⁹

The methods described were modified as follows^{28,29}:

DOPO, 54.04 g (0.25 mol), and 350 mL ethanol were filled into a 1 L three-necked round bottom flask equipped with a stirrer, a condenser and an addition funnel. The reaction mixture was heated to 70°C under stirring where as 250 mL of a 30% aqueous hydrogen peroxide solution were added drop wise over a period of 30 min. During the addition, an intense gas formation was visible, while the reaction mixture color turned to light yellow. After the complete addition of the aqueous hydrogen peroxide solution, the reaction mixture was maintained at about 80°C for an additional 12 h. The reaction mixture was concentrated by distillation, resulting in the precipitation of the product. The product was filtered, washed thoroughly with ethanol, and dried under vacuum (15 hPa) at 120°C for 24 h. The yield of DOPO-OH was 91%.

¹H-NMR (DMSO-d₆): 10.77 ppm (s, 1H); 8.06 ppm (m, 2H); 7.85 to 7.65 ppm (m, 2H); 7.50 ppm (m, 1H); 7.36 ppm (m, 1H); 7.21 ppm (t, 2H).

³¹P-NMR (DMSO-d₆): 7.2 ppm (s).

HRMS: found: 232.0267 u; calc.: 232.0289 u.

Preformulation of flame-retardant epoxy resins

Many prepolymers and their synthetic methods are discussed in literature.^{7,30-34} DEN 438, 100.0 g, were

fed into a 100 mL round bottom flask and heated up to 120°C under vacuum (5×10^{-2} hPa) for 1 h to remove all volatile impurities. To this resin, 0.1% of triethanolamine as a catalyst and the phosphorus-containing flame retardant were added. The reaction mixtures were stirred for 1 h at 150°C. The formulations are summarized in Table I for DOPO and its derivatives, in Table II for DPPO and its derivatives, and in Table III for diphenyl phosphite and diphenyl phosphate. Applying this manufacturing process, several series of prepolymers with a phosphorus content from 0.5 to 2.0% were obtained.

Curing procedure

The epoxy equivalent weight (EEW) of each flame-retardant epoxy resin was quantified. DDM was used as a hardener. The reactants were mixed at a stoichiometrical ratio of 1 : 0.5 (epoxy groups: amino groups). These mixtures were heated on a hot plate to about 120°C with constant stirring until complete homogeneity was observed. Then, the resins were cured at 140°C for 2 h and postcured at 200°C for 2 h. The samples were allowed to cool down slowly to room temperature.

RESULTS AND DISCUSSION

Even though DOPO and DPPO had been examined^{16,17,35,36} before, the crystal structures of both have not yet been published. Single crystals for XRD analysis were obtained by recrystallization of DPPO out of benzene and, respectively, DOPO out of toluene.

TABLE II
Overview of the Actual Compositions of the Synthesized Flame-Retardant Epoxy Resins
Based on DPPO and Its Derivatives

Number	DEN (g)	DPPO (g)	DPPO-OH (g)	DPPO-CH ₂ OH (g)	Catalyst (g)	Phosphorus content (% P)	Flame retardant content (%)
4-1	100.00	4.10			0.1	0.50	3.9
4-2	100.00	6.27			0.1	0.75	5.9
4-3	100.00	8.54			0.1	1.00	7.9
4-4	100.00	10.91			0.1	1.25	9.8
4-5	100.00	13.39			0.1	1.50	11.8
4-6	100.00	18.68			0.1	2.00	15.7
5-1	100.00		4.38		0.1	0.50	4.2
5-2	100.00		6.71		0.1	0.75	6.3
5-3	100.00		9.15		0.1	1.00	8.4
5-4	100.00		11.71		0.1	1.25	10.5
5-5	100.00		14.39		0.1	1.50	12.6
5-6	100.00		20.16		0.1	2.00	16.8
6-1	100.00			4.62	0.1	0.50	4.4
6-2	100.00			7.10	0.1	0.75	6.6
6-3	100.00			9.70	0.1	1.00	8.8
6-4	100.00			12.42	0.1	1.25	11.0
6-5	100.00			15.28	0.1	1.50	13.2
6-6	100.00			21.47	0.1	2.00	17.7

The detailed crystal data is summarized in Table IV. The structures of DPPO and DOPO are presented in Figures 5 and 6.

Obviously, both DOPO and DPPO, have a central six-membered ring, consisting of four aromatic carbon atoms, one oxygen, and one phosphorus atom. Although the oxidation states according to the electronegativities of Pauling are the same for both phosphorus atoms, their chemical environment is different in both compounds: DPPO is a phosphine oxide, while DOPO is a phosphinic acid ester.

DOPO consists of a three-ring system similar to phenanthrene. The DPPO molecule looks like a buckled anthracene. The endocyclic angle between C1—O1—C1' is 121.8°. However, the angle of torsion defined by O1—C1—C6—P1 (central ring) is 1.9°. Although the middle ring is not ideally planar, the

bond length between the oxygen (O1) and the two carbon atoms of the adjacent rings (C1 and C1') has a length of 138.0 pm. Therefore the both aromatic rings seem to be conjugated over the oxygen bridge. In comparison to this the carbon-oxygen bond (C12/O1) in the DOPO molecule; however, has a length of 141.1 pm and is in the same range of typical carbon-oxygen single bonds.^{37,38} The phosphorus - hydrogen bonds in both molecules have nearly the same length. This explains their similar chemical reactivity as regards the addition reaction with aldehydes and oxidation.

There are some possible modes of action of all classes of flame retardants, like charring, including intumescence, cooling and dilution, and radical inhibition mechanisms in the gas phase.^{5,7}

The formation of the PO radicals on exposure to heat as the main degradation route of DOPO was

TABLE III
Overview of the Actual Compositions of the Synthesized Flame-Retardant Epoxy Resins
Based on Diphenyl Phosphite and Diphenyl Phosphate

Number	DEN [g]	Diphenyl phosphite (g)	Diphenyl phosphate (g)	Catalyst (g)	Phosphorus content (% P)	Flame retardant content (%)
7-1	100.00	3.92		0.1	0.50	3.8
7-2	100.00	6.00		0.1	0.75	5.7
7-3	100.00	8.16		0.1	1.00	7.5
7-4	100.00	10.42		0.1	1.25	9.4
7-5	100.00	12.77		0.1	1.50	11.3
7-6	100.00	17.78		0.1	2.00	15.1
8-1	100.00		4.20	0.1	0.50	4.0
8-2	100.00		6.44	0.1	0.75	6.0
8-3	100.00		8.77	0.1	1.00	8.1
8-4	100.00		11.21	0.1	1.25	10.1
8-5	100.00		13.76	0.1	1.50	12.1
8-6	100.00		19.23	0.1	2.00	16.1

TABLE IV
Crystal Data and Structure Refinement of 2,8-Dimethyl-phenoxaphosphin-10-oxide (DPPO) and 9,10-Dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO)

	DPPO	DOPO
Empirical formula	C ₁₄ H ₁₃ O ₂ P ₁	C ₁₂ H ₉ O ₂ P ₁
Formula weight	244.21	216.16
Crystal system, space group	monoclinic, P2 ₁ (No. 4)	orthorhombic, P2 ₁ 2 ₁ 2 ₁ (No. 19)
Unit cell dimensions	<i>a</i> = 4.2851(4) Å <i>b</i> = 10.2437(11) Å <i>c</i> = 13.4744(14) Å A = 90° β = 96.9810(10)° γ = 90°	<i>a</i> = 4.6074(17) Å <i>b</i> = 12.889(5) Å <i>c</i> = 16.465(6) Å α = 90° β = 90° γ = 90°
Volume	587.08(10) Å ³	977.8(6) Å ³
Z, calculated density	2, 1.382 (Mg/m ³)	4, 1.468 (Mg/m ³)
Crystal size	0.4 × 0.4 × 0.25 mm ³	0.3 × 0.3 × 0.1 mm ³
Wavelength	0.71073 Å	0.71073 Å
Absorption coefficient	0.219 mm ⁻¹	0.253 mm ⁻¹
Final R indices [I > 2σ (I)]	R ₁ = 0.0377 ωR ₂ = 0.0936	R ₁ = 0.0756 ωR ₂ = 0.1970
R indices (all data)	R ₁ = 0.0425 ωR ₂ = 0.0955	R ₁ = 0.1235 ωR ₂ = 0.2295

discussed before.^{39,40} The main product during the formation of the PO radicals from DOPO is supposed to be dibenzofuran, which is aromatic. 2,8-dimethylbenzofuran is produced in the case of the thermal degradation of DPPO.

The fragmentation during mass spectroscopy to find these compounds has been retraced. The fragmentation schemes of DPPO and DOPO are shown in Figure 7. The main degradation route of both starts with the homolytical cleavage of the P—H bond. The resulting radicals stabilize themselves by forming a dibenzofuran system and separating the PO radical. This degradation route is confirmed by the DFT calculations presented earlier.³⁹ These calculations revealed, with DOPO being used as an example, the direct break-up into dibenzofuran and the HPO molecule is not thermodynamically favored. On the other hand, it was shown that the decay of the P—H bond, followed by the degradation of the

formed radical into dibenzofuran and the PO radical, is energetically preferred.

In addition, the pyrolysis gases of cured resins with and without flame retardants were analyzed by thermal desorption mass spectroscopy. The results are presented in Figure 8. The DOPO- and DPPO-containing polymers showed a significant release of the PO radical (47 amu). The virgin DEN cured with DDM and the diphenyl phosphite-containing sample emitted only traces of this mass. Pyrolysis of the tested epoxy resins starts at about 325°C, as carbon dioxide is detected at this temperature. The emission of PO reaches its maximum at about 400 to 450°C. The DOPO-containing crosslinked epoxy resin released more PO than the DPPO-containing one. This

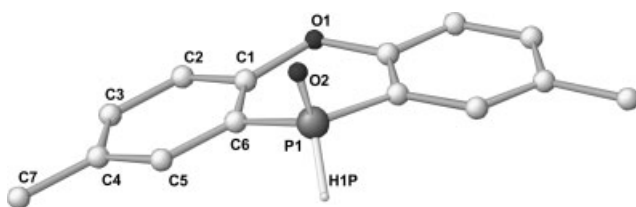


Figure 5 Crystal structure of DPPO and selected bond lengths [Å]: P(1)-O(2) 1.4894,(15) P(1)-C(6) 1.783,(2) O(1)-C(1) 1.380,(3) C(4)-C(7) 1.505,(3) C(5)-C(6) 1.406,(3) P(1)-H(1P) 1.270(0); angles [°]: O(2)-P(1)-C(6) 115.78,(9) O(2)-P(1)-C(6) 115.78,(9) O(1)-C(1)-C(6) 124.82,(19) C(5)-C(6)-P(1) 120.19,(16) C(1)-O(1)-C(1') 121.8; angles of torsion [°]: O1-C1-C6-P1: 1.9, C1-C6-P1-C1': -18.5. Single crystals for XRD were obtained by recrystallization from benzene.

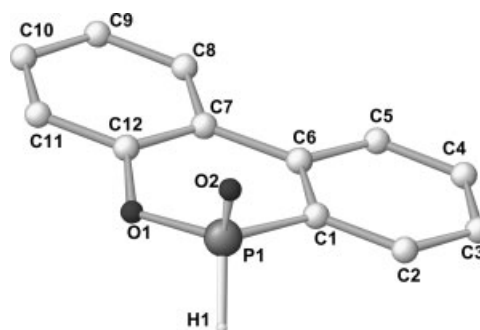


Figure 6 Crystal structure of DOPO and selected bond lengths [Å]: P(1)-O(2) 1.474,(4) P(1)-O(1) 1.549,(4) P(1)-C(1) 1.784,(4) O(1)-C(12) 1.411,(5) C(1)-C(2) 1.382,(6) C(1)-C(6) 1.403,(6) C(2)-C(3) 1.368,(6) C(6)-C(7) 1.481,(6); angles [°]: O(2)-P(1)-O(1) 112.2,(3) O(2)-P(1)-C(1) 116.1,(2) O(1)-P(1)-C(1) 105.3,(2) C(12)-O(1)-P(1) 125.1,(3) C(2)-C(1)-C(6) 120.8(4); angle of torsion [°]: C1—P1—O1—C12: -25.4. Single crystals for XRD were obtained by recrystallization from toluene.

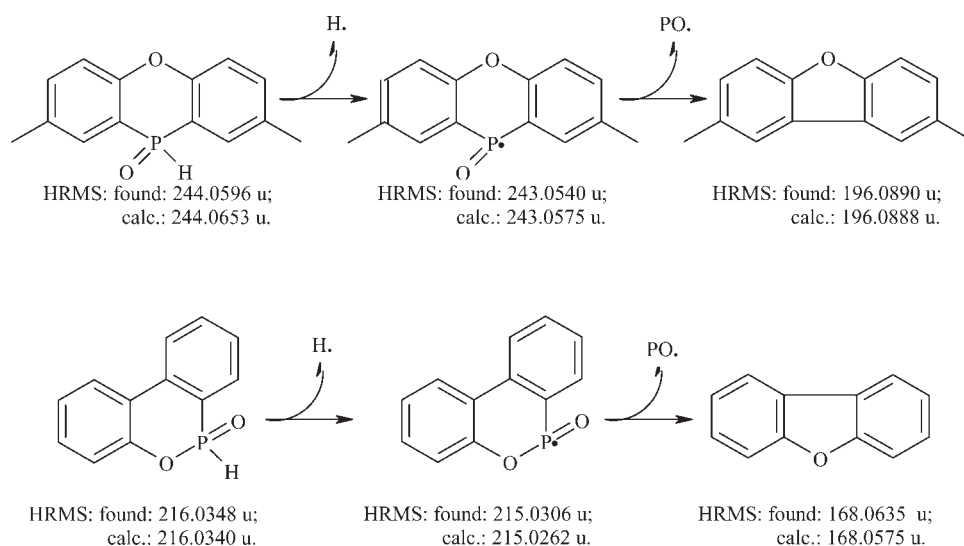


Figure 7 Fragmentation scheme of DPPO and DOPO.

may explain the slight differences in flame retardancy described below. HPO (48 amu) was not detected in any measured sample.

According to literature,^{40–42} the PO radical interacts with H and OH radicals in the gaseous phase of the fire (Fig. 9). Both radicals are known to be species maintaining polymer degradation and combustion.

The thermal desorption mass spectroscopy measurements confirm the presented fragmentation scheme of DOPO and DPPO (Fig. 7). Formation of the benzofurans and PO radical depends either on the combustion temperature (Fig. 8) and the polymer matrix.

All prepolymers were cured with DDM as described above. The glass transition temperatures (T_g) were obtained via DSC and plotted against the phosphorus contents of the cured flame-retardant epoxy resins (Figs. 10–13). The results of these flammability tests are summarized in Tables V–VII.

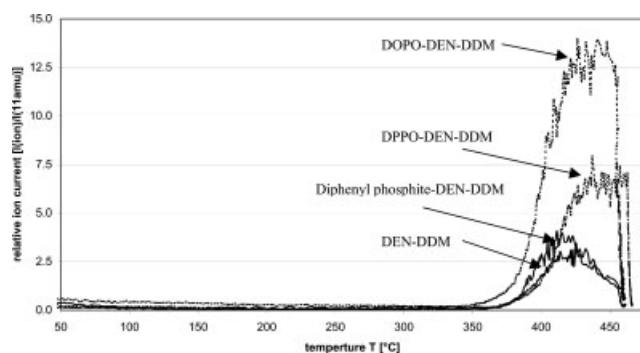


Figure 8 Thermal desorption mass spectrum of the DDM cured resins.

The glass transition temperature of virgin epoxy novolac (DEN 438) cured with DDM was 218°C. This unmodified epoxy novolac had no rating in the UL 94 vertical burning test.

All assayed additives based on DOPO and DPPO appeared to be very effective flame retardants, as all cured samples had been rated UL 94 V0 with phosphorus contents of about 0.8% in the formulation (Tables V and VI). The two reference phosphorus compounds, which do not have the heterocyclic structure, have no flame-retardant effect, as the samples with a phosphorus content of 1.7% failed the UL 94 vertical burning test (Table VII).¹² The maximum phosphorus concentration in the corresponding preformulations was 2.0%. Higher phosphorus contents could not be reached, because higher loadings could not be processed because of the fact that the decomposition temperature was lower than the melting point of these preformulations.

Direct comparison of the UL 94 ratings of the DOPO- and DPPO-based epoxies showed that the V1 rating was achieved with DOPO at a phosphorus content of 0.4%, while no classification was possible in the case of DPPO. Moreover, the DPPO series revealed the straight transition to V0 at a phosphorus content of 0.6%, whereas DOPO needed 0.8% P to achieve the same rating.

In the case of the oxidized compounds (DOPO—OH and DPPO—OH), the V1 rating was observed at 0.6% P for DOPO—OH. DPPO—OH achieved the V0 rating directly at 0.8% P, as did the DOPO—OH.

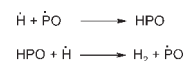


Figure 9 Possible mechanism of radical scavenging by the PO radical.³⁹

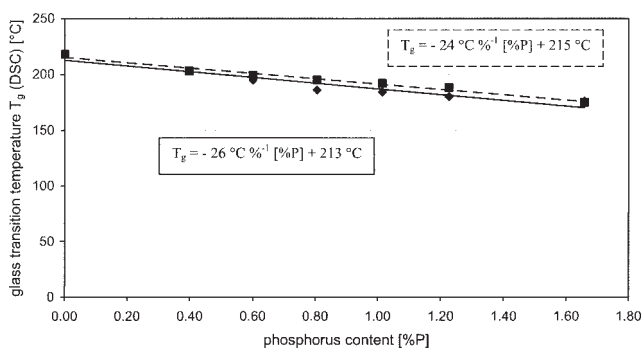


Figure 10 T_g versus phosphorus content and the linear regressions for the flame-retardant epoxy resins based on the unmodified flame retardants: ■ / - - - for DPPO and ◆ / — for DOPO.

Both formaldehyde-modified derivatives reached the V1 rating at the same phosphorus content of 0.4%. The flame-retardant effect of DPPO-CH₂OH again seemed to be better than that of the DOPO-CH₂OH: only 0.6% P were needed to be classified as V0 compared to 0.8% P (Tables V and VI). In spite of these differences the efficiency of DOPO, DPPO, and their derivatives is nearly identical.

The series containing the two nonheterocyclic phosphorus compounds - diphenyl phosphite and diphenyl phosphate - did not meet the requirements for a rating according to the UL 94 test.

The burning behavior of all resin systems were also characterized by the lowest oxygen index (LOI). The results are summarized in Tables V–VII. In general, the increasing flame-retardant content, leading to an increasing phosphorus content, made a higher oxygen concentration necessary to allow for combustion of the samples, which is the LOI.

Although DPPO and DOPO have nearly the same performance in the UL 94 test, the LOI values differ significantly. Obviously, DOPO and its derivatives showed a better performance in this testing proce-

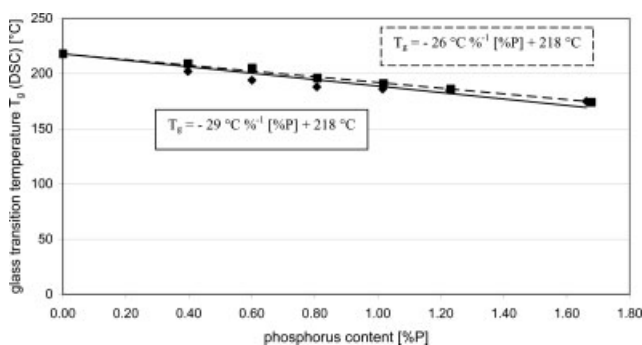


Figure 11 T_g versus phosphorus content and the linear regressions for the flame-retardant epoxy resins based on the oxidized flame retardants: ■ / - - - for DPPO-OH and ◆ / — for DOPO-OH.

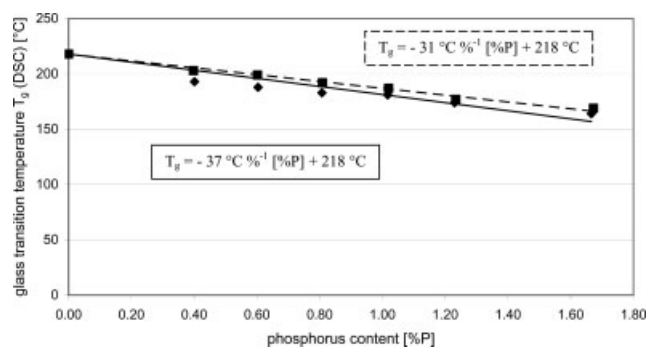


Figure 12 T_g versus phosphorus content and the linear regressions for the flame-retardant epoxy resins based on the formaldehyde-modified flame retardants: ■ / - - - for DPPO-CH₂OH and ◆ / — for DOPO-CH₂OH.

sure than DPPO. Direct comparison of the equivalent derivatives at the highest phosphorus content (2.0% in the preformulation, about 1.7% in the cured material) revealed that the DOPO-containing samples needed in the LOI rating 6.8 (unmodified), 3.4 (OH-functionalised), and 8.1 more oxygen than the DPPO-containing ones, respectively.

At very low phosphorus contents (0.4%) in DDM-cured samples containing DPPO and DPPO-OH, the LOI was lower, than that of virgin DEN 438. This is due the incorporation of flame retardants inhibiting the formation of a perfect crosslinked polymer, as the reactive flame retardants are bound to epoxy groups. This also affects the glass transition temperatures and will be discussed below. With increasing phosphorus amounts the flame-retardant effect of the added compounds is dominating.

Comparison of the heterocyclic flame retardants with diphenyl phosphite and diphenyl phosphate confirmed the UL 94 test results, as the LOI values of the latter two compounds are lower than that of the virgin DDM-cured epoxy novolac. Both showed

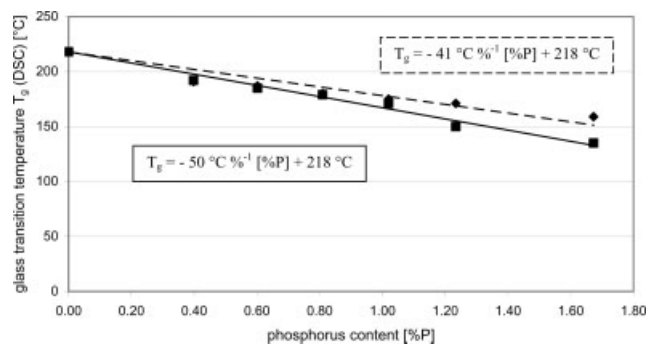


Figure 13 T_g versus phosphorus content and the linear regressions for the flame-retardant epoxy resins based on the reference phosphorus-containing compounds: ■ / - - - for diphenyl phosphate and ◆ / — for diphenyl phosphite.

TABLE V
UL 94 Rating and LOI of the DDM-Cured Flame-Retardant Epoxy Resins Based on DOPO and its Derivatives

DOPO	Phosphorus content (%P)			Phosphorus content (%P)			Phosphorus content (%P)		
	UL 94 rating	LOI	DOPO-OH	UL 94 Rating	LOI	DOPO-CH ₂ OH	UL 94 rating	LOI	
1-0	no V rating	26.5	2-0	no V rating	26.5	3-0	no V rating	26.5	
1-1	V1	28.2	2-1	no V rating	27.9	3-1	V1	28.7	
1-2	V1	29.3	2-2	V1	31.2	3-2	V1	31.1	
1-3	V0	31.5	2-3	V0	31.6	3-3	V0	33.5	
1-4	V0	32.8	2-4	V0	32.1	3-4	V0	34.7	
1-5	V0	33.4	2-5	V0	32.8	3-5	V0	36.1	
1-6	V0	35.7	2-6	V0	33.9	3-6	V0	39.2	

TABLE VI
UL 94 Rating and LOI of the DDM-Cured Flame-Retardant Epoxy Resins Based on DPPO and its Derivatives

DPPO	Phosphorus content (%P)			Phosphorus content (%P)			Phosphorus content (%P)		
	UL 94 rating	LOI	DPPO-OH	UL 94 rating	LOI	DPPO-CH ₂ OH	UL 94 rating	LOI	
4-0	no V rating	26.5	5-0	no V rating	26.5	6-0	no V rating	26.5	
4-1	no V rating	25.4	5-1	no V rating	25.8	6-1	V1	27.1	
4-2	V0	26.6	5-2	no V rating	27.1	6-2	V0	27.9	
4-3	V0	27.4	5-3	V0	27.9	6-3	V0	28.3	
4-4	V0	27.8	5-4	V0	28.5	6-4	V0	28.6	
4-5	V0	28.3	5-5	V0	29.2	6-5	V0	29.1	
4-6	V0	28.9	5-6	V0	30.5	6-6	V0	31.1	

TABLE VII
UL 94 Rating and LOI of the DDM-Cured Flame-Retardant Epoxy Resins Based on Diphenyl Phosphite and Diphenyl Phosphate

Diphenyl phosphite	Phosphorus content (%P)	UL 94 rating	LOI	Diphenyl phosphate	Phosphorus content (%P)	UL 94 rating	LOI
7-0	0.00	no V rating	26.5	8-0	0.00	no V rating	26.5
7-1	0.40	no V rating	25.4	8-1	0.40	no V rating	26.1
7-2	0.60	no V rating	24.9	8-2	0.60	no V rating	25.5
7-3	0.81	no V rating	24.3	8-3	0.81	no V rating	24.2
7-4	1.02	no V rating	23.4	8-4	1.02	no V rating	25.8
7-5	1.23	no V rating	24.8	8-5	1.23	no V rating	26.4
7-6	1.67	no V rating	26.1	8-6	1.67	no V rating	27.3

a minimum at around 0.8% P to 1.0% P and reached the value of the unmodified novolac at about 1.7% P.

Although the defragmentation conditions in the mass spectrometer are not identical with the real combustion behavior, the HRMS gives an idea of the possible products formed during the energetical decomposition of a compound. Thermal desorption mass spectroscopy clearly confirmed the formation of PO radicals in the case of the pyrolysis of DOPO- and DPPO-containing epoxy resins.

It is likely that DPPO and DOPO take a different way of decomposition and way of action than the nonheterocyclic compounds tested. DOPO and DPPO release the stable dibenzofuran and 2,8-dimethyl-dibenzofuran, respectively, under thermal decomposition and as a result, the small phosphorus-containing PO radical is formed. Diphenyl phosphite and diphenyl phosphate do not have the possibility to form PO during decomposition. The difference of DOPO- and DPPO-containing resins may be due to the fact that DOPO containing polymers showed a higher PO release during thermal decomposition.

The incorporation of flame retardants in epoxy resin systems normally leads to a reduction of the glass transition temperature (T_g) of the cured polymer.^{43–45} This phenomenon was observed in all test series studied.

All additives were bound covalently to the epoxy resin. Hence, every flame-retardant molecule consumed one epoxy group in the preformulation reaction. This led to a decreasing number of the epoxy groups, while the flame retardant content increased (Figs. 2 and 3). The consequence was an increase of the epoxy equivalent number (defined as the mass per equivalent oxirane). The crosslinking density significantly depended on the concentration of epoxy groups. The sample with the highest crosslinking density was the DDM-cured virgin epoxy novolac. Its glass transition temperature was 218°C. With increasing flame retardant content, the phosphorus concentration increased, leading to a decreasing crosslinking density and, hence, to a decreasing T_g . It must be noted that the decrease of T_g is quite lin-

ear to the phosphorus content of the flame-retardant epoxy resins, as linear regressions were applied accordingly to all series presented here.

The T_g found for the V0-rated samples were high, higher than 180°C for all of the DOPO- and DPPO-based flame-retardant epoxy resins. This is due to the fact that samples with these two flame retardants needed only very low phosphorus contents (about 0.8%). This phosphorus content corresponded to an amount of ~ 7–8 mass percent in the preformulation.

In general, the DPPO samples appeared to have a glass transition temperature that exceeded that of the comparable DOPO derivatives by about 10°C. All samples with a phosphorus content of 1.7% showed a very similar glass transition temperature of around 170°C. The two reference compounds-diphenyl phosphite and diphenyl phosphate - exhibited a much lower glass transition temperature (Figs. 10–13).

CONCLUSIONS

The single-crystal structures, spectral data, and thermal properties of DPPO and DOPO were obtained.

DOPO and its analog were modified by oxidation and addition of formaldehyde. All six components were incorporated in epoxy novolac to form flame-retardant epoxy resins. The same incorporation was performed with diphenyl phosphite and diphenyl phosphate.

After curing with DDM, all resins containing DPPO, DOPO or one of their derivatives had the classification UL 94 V0 at a phosphorus content of 0.8% in the formulation. Although DPPO and DPPO-CH₂OH achieved this rating at 0.6% P, the flame-retardant efficiency seemed to be quite similar. The diphenyl phosphite and its oxidized form (diphenyl phosphate) exhibited no significant flame-retardant effect at a phosphorus content of up to 1.7% in the final formulation.

Epoxy resins incorporating DOPO-based flame retardants showed high oxygen indices of up to 39.2% O₂ at a phosphorus content of 1.7%, while DPPO-based ones exhibited LOI values of up to

31.1% at comparable phosphorus contents. The modification of epoxy novolac with diphenyl phosphite and diphenyl phosphate led to a lowering of the LOI at low phosphorus contents and then to a slow rising, but did not significantly outreach the virgin DDM-cured novolac.

The modes of action of heterocyclic and non heterocyclic phosphorus containing polymers were examined by high-resolution mass spectroscopy and thermal desorption mass spectroscopy. During the decomposition of DOPO and DPPO the main product dibenzofuran and, respectively, 2,8-dimethyldibenzofuran were detected. Thermal desorption mass spectroscopy lead to the direct detection of the PO radical. Unmodified and diphenyl phosphite containing epoxy resins did not emit this volatile compound.

However, the glass transition temperatures of the V0-rated polymers were approximately 185°C for the DOPO-based resins and approximately 195°C for the DPPO ones. These promising results allow the testing of DPPO and its derivatives in other polymer matrices.

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