

# Phosphorus-Containing Terephthaldialdehyde Adducts—Structure Determination and their Application as Flame Retardants in Epoxy Resins

S. Seibold,<sup>1</sup> A. Schäfer,<sup>1</sup> W. Lohstroh,<sup>2</sup> O. Walter,<sup>1</sup> M. Döring<sup>1</sup>

<sup>1</sup>Karlsruhe Research Centre, Institute for Technical Chemistry, Hermann-von-Helmholtz-Platz 1, D-76344 Eggenstein-Leopoldshafen, Germany

<sup>2</sup>Karlsruhe Research Centre, Institute for Nanotechnology, Hermann-von-Helmholtz-Platz 1, D-76344 Eggenstein-Leopoldshafen, Germany

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**ABSTRACT:** Two novel phosphorus-rich prepolymers based on epoxy novolac and terephthaldialdehyde and potential flame retardants, 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO) and 2,8-dimethyl-phenoxaphosphin-10-oxide (DPPO) were synthesised. The resultant flame-retardant epoxy resins were cured with 4,4'-diaminodiphenylmethane (DDM) and 4,4'-diamino-dicyclohexylmethane (PACM). Their flammability and burning behavior were characterised by UL 94 and LOI and compared with analogue prepolymers based on diethylphosphite (DEPP). The glass transition temperatures were determined by DSC measurements. Furthermore, the structures of two exem-

plary molecules based on *p*-tolylaldehyde adducts were examined by XRD and NMR analysis to determine the possibilities of linking the two novel DOPO and DPPO derivatives to the backbone of the epoxy resin. Additionally, the char yields were determined by TG analysis and thermal desorption mass spectroscopy of the thermosets used and compared with each other to obtain more information about the possible mode of flame-retardant action of the different phosphorus compounds. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 108: 264–271, 2008

**Key words:** flame retardance; resins; crystal structure

## INTRODUCTION

Epoxy resins are one of the most versatile classes of polymers. Their long service life and good physical and chemical properties often provide a favourable cost benefit ratio when compared with other thermosets.<sup>1,2</sup> When listing their advantages, the high flammability of epoxy resins certainly has to be considered a major disadvantage.

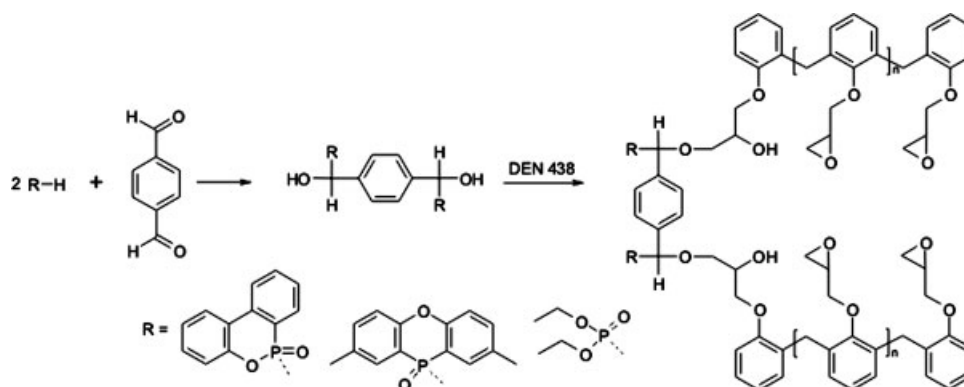
Fire retardant epoxy resins are required in fields of electronic and electrical applications (printed-circuit boards, encapsulations) and transportation (automobiles, trains, and military and civilian aircraft).<sup>3–7</sup> Therefore, cured epoxy resins containing bromine are particularly useful when flame retardancy is desired. The resins in use mainly contain tetra-bromobisphenol A (TBBPA). However, major problems encountered with this system include the generation of toxic and corrosive fumes during combustion and waste disposal. This led to the search

for alternative flame retardants. Organophosphorus compounds like 9,10-dihydro-9-oxa-phosphaphenanthrene-10-oxide (DOPO) introduced in the 70s generate less toxic gases and smoke than halogen-containing compounds and also exhibit high flame-retardant effects when incorporated into epoxy resins.<sup>8–10</sup> A common derivative of DOPO is the adduct of DOPO and *p*-benzoquinone—the 2-(10-oxo-10H-9-oxa-10λ<sup>5</sup>-phosphaphenanthrene-10-yl)-benzene-1,4-diol (DOPO-HQ). This bifunctional flame retardant is also commercially available and used for printed-circuit board composites.

The present article will focus on the synthesis and characterization of novel phosphorus-rich bifunctional flame retardants, on their incorporation in the backbone of epoxy resins, and on studying their burning behavior. For this purpose the adducts of the phosphacyclic DOPO and DPPO with terephthaldialdehyde (TDA) were synthesised and the resultant bifunctional substances similar to the known DOPO-HQ were incorporated in the epoxy backbone of an epoxy novolac (Fig. 1). The resins were cured with 4,4'-diaminodiphenylmethane (DDM) and 4,4'-diamino-dicyclohexylmethane (PACM). The cured thermosets were characterized by the UL 94 test, limiting oxygen index (LOI), and differential scanning calorimetry (DSC) and compared with analogue thermosets

Correspondence to: M. Döring (manfred.doering@itc-cpv.fzk.de).

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**Figure 1** Synthesis paths of flame-retardant epoxy resins based on DOPO<sub>2</sub>-TDA, DPPO<sub>2</sub>-TDA, and DEPP<sub>2</sub>-TDA ( $n = 1.6$ ).

based on the TDA adduct of diethylphosphite (DEPP) (Fig. 1). To determine the exact structure of the new flame retardants and their abilities to link covalently to the backbone of the epoxy resin, DPPO and DOPO were reacted with *p*-tolylaldehyde to form exemplary substances (DOPO-TA and DPPO-TA) for chemical characterisation. The structures of the latter two substances were accurately determined by XRD analysis and their NMR data compared with the NMR data were of the insoluble DOPO and DPPO TDA adducts.

## EXPERIMENTAL

### Materials and reagents

Toluene, 1,4-diazabicyclo[2.2.2]octane (DABCO), DEPP, TDA, acetonitril, dimethylsulfoxide (DMSO), *p*-tolylaldehyde, and 4,4'-diaminodiphenylmethane (DDM), were purchased from Aldrich and used without any further purification. Triethanolamine was from VWR. Epoxy phenol novolac (DEN 438) was used from DOW AG. The 9,10-dihydro-9-oxa-phosphaphenanthrene-10-oxide (DOPO) was supplied by Schill und Seilacher AG. The 4,4'-diamino-dicyclohexylmethane (PACM) was kindly donated by Air Products GmbH. The 2,8-dimethyl-phenoxaphosphin-10-oxide (DPPO) was synthesised as presented earlier.<sup>11–13</sup>

### Measurement and testing

<sup>1</sup>H and <sup>31</sup>P NMR spectra were obtained by a Bruker Analytical BZH 250/52 Spectrometer at 250 MHz. Samples were analyzed in deuterated DMSO or CDCl<sub>3</sub>.

Differential scanning calorimeter (DSC) measurements were done using a Mettler–Toledo DSC 822<sup>e</sup> at a scan rate of 20°C/min.<sup>14</sup>

Thermogravimetry measurements were performed with a Mettler–Toledo TGA/SDTA 851<sup>e</sup> at a scan rate of 10°C/min under nitrogen. Every measurement was performed with ~ 5 mg.

The UL 94 vertical burning classification was obtained using an ATLAS HVUL 2 burning chamber

according to DIN IEC 60695-11-10 with a 50-W burner flame. The sample thickness was (7 ± 1) mm.<sup>15</sup>

The LOI was obtained with an FTT LOI burning chamber according to ISO 4589 – 2.<sup>16</sup>

Thermal desorption mass spectroscopy (TD-MS) was performed in a vacuum chamber coupled to a heatable sample carrier 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 to 20 mg) were applied to the sample carrier and the system was evacuated (10<sup>-8</sup> hPa). The cured resins were heated from room temperature to 500°C at a heating rate of 10°C/min and the pyrolysis gases were detected with the mass spectrometer. The path length from the sample carrier to the detector was about 50 cm.

X-ray analysis was performed using a Siemens SMART CCD 1000 diffractometer with an irradiation time of 10 to 20 s per frame, thus collecting a full sphere of data using an  $\omega$ -scan technique with  $\Delta \omega$  ranging from 0.3° to 0.45°. Experimental absorption correction was performed with SADABS.<sup>17</sup>

Crystallographic data of the structures were deposited at the Cambridge crystallographic database centre (CCDC), supplementary publications Nos. 656271 and 656272. Structure solution and refinement were performed with SHELX 97.<sup>18</sup>

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).

Epoxy equivalent weights of epoxy resins and preformulations were determined by the hydrogen bromine method described by Lee and Neville.<sup>3</sup>

### Synthesis of 10-oxa-4b,8a,10,10a-tetrahydro-4aH-9oxa-10λ<sup>5</sup>-phospha-phenanthrene-10yl)-*p*-tolyl-methanol (DOPO-TA)

DOPO (21.6 g, 0.1 mol), 12.0 g (0.1 mol) *p*-tolylaldehyde, and 100 mL toluene were fed into a 250 mL three-necked round bottom flask equipped with a

stirrer and a condenser. The reaction mixture was stirred and refluxed carefully at 110°C for 6 h. The reaction mixture was reduced in volume by distillation, resulting in the precipitation of the product. The solid was filtered and washed with toluene. The product was recrystallized from DMSO/H<sub>2</sub>O to yield single crystals for XRD analysis. The yield was 87%.

<sup>1</sup>H NMR (DMSO-d<sub>6</sub>): 8.175 ppm (m, 2H); 7.957 ppm (m, 1H); 7.778 ppm (m, 1H); 7.607 ppm (m, 1H); 7.426 ppm (m, 2H); 7.262 to 7.113 ppm (m, 5H); 6.315 ppm (m, 1H); 5.210 ppm (dd, 1H); 2.265 ppm (s, 3H).

<sup>31</sup>P NMR (DMSO-d<sub>6</sub>): 32.207 ppm (s).

#### Synthesis of 10-oxa-10,10a-dihydro-4aH-10λ<sup>5</sup>-phenoxaphosphon-10yl)-*p*-tolyl-methanol (DPPO-TA)

DPPO (24.4 g, 0.1 mol), 12.0 g (0.1 mol) *p*-tolylaldehyde, and 100 mL toluene were fed into a 250 mL three-necked round bottom flask equipped with a stirrer and a condenser. The reaction mixture was stirred and heated carefully to 110°C for 4 h. The reaction mixture was reduced in volume by distillation, resulting in the precipitation of the product. The solid was filtered and washed with toluene. The product was recrystallized from DMSO/H<sub>2</sub>O to yield single crystals for XRD analysis. The yield was 83%.

<sup>1</sup>H NMR (DMSO-d<sub>6</sub>): 7.721 ppm (m, 2H); 7.467 ppm (m, 2H); 7.222 ppm (m, 3H); 6.959 ppm (m, 2H); 6.824 ppm (m, 1H); 6.144 (m, 1H); 5.169 (m, 1H); 2.492 (s, 3H); 2.396 (s, 3H); 2.190 (s, 3H).

<sup>31</sup>P NMR (DMSO-d<sub>6</sub>): 9.655 ppm (s).

#### Synthesis of DOPO<sub>2</sub>-TDA

The method suggested<sup>19</sup> was modified as follows: DOPO (216.17 g, 1.0 mol), 67.05 g (0.5 mol) TDA, and 500 mL toluene were fed into a 1-L three-necked round bottom flask equipped with a stirrer and a condenser. The reaction mixture was stirred and heated carefully to 110°C for 4 h. During this period, the product precipitated as a white solid. After cooling down to room temperature, the product was filtered and washed with toluene. The yield was 93%.

<sup>1</sup>H NMR (DMSO-d<sub>6</sub>): 5.33 ppm (m, 2H) 6.32 ppm (m, 2H); 7.21 to 7.60 ppm (m, 12H); 7.72 ppm (m, 1H); 7.88 ppm (m, 2H); 7.96 ppm (m, 1H); 8.25 ppm (m, 4H).

<sup>31</sup>P NMR (DMSO-d<sub>6</sub>): 31.9 ppm (s).

#### Synthesis of DPPO<sub>2</sub>-TDA

DOPO (244 g, 1.0 mol), 67.05 g (0.5 mol) TDA, and 500 mL toluene were fed into a 1-L three-necked round bottom flask equipped with a stirrer and a condenser. The reaction mixture was stirred and

heated carefully to 110°C for 4 h. During this period, the product precipitated as a white solid. After cooling down to room temperature, the product was filtered and washed with toluene. The yield was 89%.

<sup>1</sup>H NMR (DMSO-d<sub>6</sub>): 7.721 ppm (m, 2H); 7.467 ppm (m, 2H); 7.211 ppm (m, 6H); 6.932 ppm (m, 6H); 6.144 ppm (m, 2H); 5.181 (m, 2H); 2.396 ppm (m, 6H); 2.190 ppm (m, 6H).

<sup>31</sup>P NMR (DMSO-d<sub>6</sub>): 9.712 ppm (s).

#### Synthesis of ({4-[(diethoxy-phosphoryl)-hydroxy-methyl]-phenyl}-hydroxy-methyl)-phosphonic acid diethyl ester (DEPP<sub>2</sub>-TDA)

The method suggested<sup>20</sup> was modified as follows: 13.81 g (0.10 mol) DEPP, 6.71 g (0.05 mol) terephthalaldehyde, 0.55 g (4.91 mmol) DABCO, and 50 mL anhydrous acetonitrile were charged into a 100 mL three-necked round bottom flask equipped with a stirrer and a condenser with exhaust pipe. The reaction mixture was stirred for 24 h at room temperature. The solvent was evaporated in vacuum giving the product as white powder. The white powder was dried under vacuum (15 hPa) at 90°C for 24 h. The yield of DEPP<sub>2</sub>-TDA was 93%.

<sup>1</sup>H NMR (d<sub>6</sub>-DMSO): 1.15 ppm (m, 12H); 3.96 ppm (m, 8H); 4.91 ppm (dd, 2H); 6.20 ppm (dd, 2H); 7.38 ppm (s, 4H).

<sup>31</sup>P NMR (CDCl<sub>3</sub>): 22.96 ppm (s).

HRMS: found: 410.1328 u; calc.: 410.1259 u.

#### Synthesis of (hydroxy-*p*-tolyl-methyl)-phosphonic acid diethyl ester (DEPP-TA)

The method suggested<sup>20</sup> was modified as follows: 13.81 g (0.10 mol) DEPP, 12.02 g (0.1 mol) *p*-tolualdehyde, 0.55 g (4.91 mmol) DABCO, and 50 mL anhydrous acetonitrile were charged into a 100 mL three-necked round bottom flask equipped with a stirrer and a condenser with exhaust pipe. The reaction mixture was stirred for 24 h at room temperature. The solvent was evaporated in vacuum at 80°C, giving the product as white crystals while cooling to room temperature. These were dried under vacuum (15 hPa) at 90°C for 24 h. The yield of DEPP-TA was 87%.

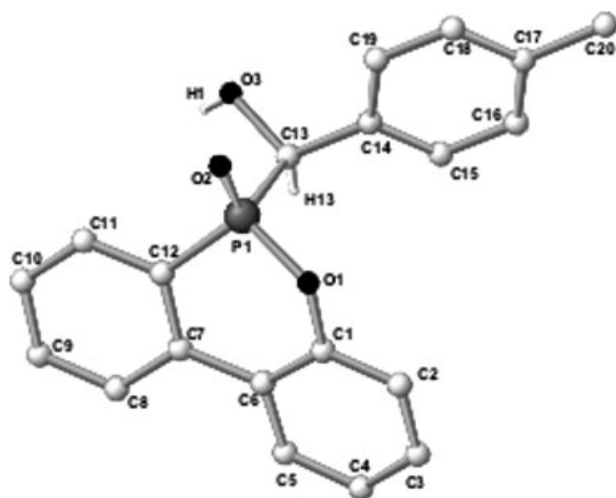
<sup>1</sup>H NMR (d<sub>6</sub>-DMSO): 1.28 ppm (tr, 6H); 1.42 ppm (tr, 3H); 4.11 ppm (m, 4H); 5.02 (d, 1H); 7.22 ppm (d, 2H); 7.42 ppm (d, 2H).

<sup>31</sup>P NMR (CDCl<sub>3</sub>): 22.97 ppm (s).

HRMS: found: 285.1062 u; calc.: 285.1021 u.

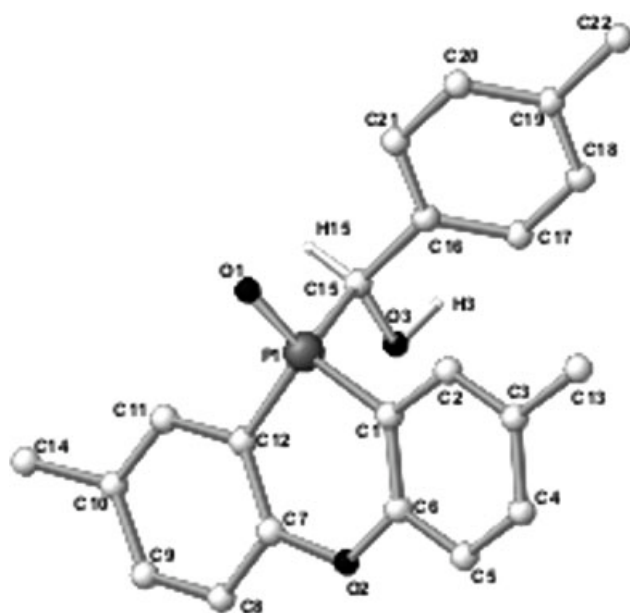
#### Preformulation of flame-retardant epoxy resins

Many prepolymers and their synthesis methods are discussed in literature.<sup>7,21-25</sup> About 100.0 g of DEN 438 were fed into a 100 mL round bottom flask and



**Figure 2** Crystal structure of the addition product of DOPO and *p*-tolyl-aldehyde (DOPO-TA) and selected bond lengths [Å]: P(1)-C(12) 1.7748, P(1)-O(2) 1.4769, P(1)-O(1) 1.6011, C(1)-O(1) 1.3936, P(1)-C(13) 1.8267, C(13)-H(13) 0.9541, C(13)-O(3) 1.4235, O(3)-H(1) 0.8370, C(13)-C(14) 1.5096; angles [°]: O(2)-P(1)-C(13) 112.87, O(3)-C(13)-H(13) 110.1, C(13)-O(3)-H(1) 105.7, P(1)-C(13)-C(14) 112.10.

heated up to 120°C under vacuum ( $5 \times 10^{-2}$  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 actual weights were calculated by applying eq. (1). In this manufacturing process, several types



**Figure 3** Crystal structure of the addition product of DPPO and *p*-tolyl-aldehyde (DPPO-TA) and selected bond lengths [Å]: C(1)-P(1) 1.783, P(1)-O(1) 1.4953, P(1)-C(15) 1.833, C(15)-O(3) 1.413, C(15)-H(15) 0.980, O(3)-H(3) 0.919, C(15)-C(16) 1.517; angles [°]: O(1)-P(1)-C(15) 108.34, P(1)-C(15)-O(3) 107.36, H(15)-C(15)-O(3) 108.3, C(15)-O(3)-H(3) 96.4.

of prepolymers with phosphorus contents from 0.5% up to 2.0% were obtained.

$$m(\text{FR}) = \frac{m(\text{resin}) \times \%P}{\frac{30.97 \text{ g mol}^{-1} \times n}{M(\text{FR})} - \%P}$$

with  $m(\text{FR})$  = mass of flame retardant,  $m(\text{resin})$  = mass of epoxy resin,  $\%P$  = target phosphorus content of the preformulation divided by 100, and  $n$  = number of phosphorus atoms per FR molecule.

Equation 1 gives formula to calculate the mass of added flame retardants.

## RESULTS AND DISCUSSION

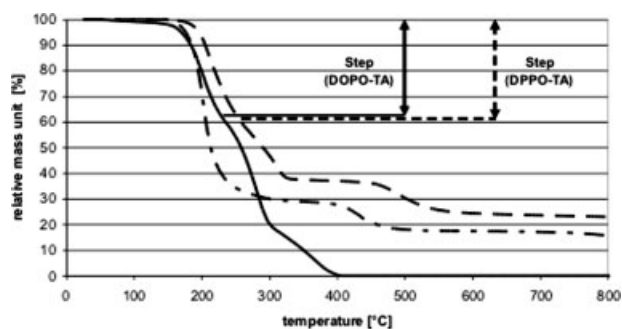
### Structure determination

The reaction of DOPO with aldehydes was described previously.<sup>24–29</sup> The added products of DOPO and its analogue DPPO and *p*-tolylaldehyde were synthesised successfully. Their chemical structures were determined by XRD and NMR analysis. The structures of these adducts are presented in Figures 2 and 3, while the detailed crystal data can be obtained from Table I.

DOPO and DPPO are isomeric molecules. Except for the two methyl groups bound to the aromatic carbocycles, they have the same empirical formula. The three-ring system of the DOPO molecule resembles phenanthrene, while DPPO looks similar to an anthracene. Furthermore, DOPO is a phosphinic acid

**TABLE I**  
Crystal Data and Structure Refinement of (2,8-Dimethyl-10-oxo-10H-10λ<sup>5</sup>-Phenoxaphosphin-10-yl)-*p*-Tolyl-Methanol (DPPO-TA) and (10-oxo-10H-9-oxa-10λ<sup>5</sup>-Phosphaphenanthrene-10-yl)-*p*-Tolyl-Methanol (DOPO-TA)

|                                   | DPPO-TA   | DOPO-TA   |
|-----------------------------------|---|---|
| Empirical formula                 | C <sub>22</sub> H <sub>21</sub> O <sub>3</sub> P <sub>1</sub>   | C <sub>20</sub> H <sub>17</sub> O <sub>3</sub> P <sub>1</sub>   |
| Formula weight                    | 364.36  | 336.31  |
| Crystal system,                   | orthorhombic,   | orthorhombic,   |
| space group                       | Pna2 <sub>1</sub> (No. 33)  | P2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub> (No. 19)  |
| Unit cell dimensions              | $a = 12.4856(9) \text{ \AA}$<br>$\alpha = 90^\circ$<br>$b = 13.3976(10) \text{ \AA}$<br>$\beta = 90^\circ$<br>$c = 11.2126(8) \text{ \AA}$<br>$\gamma = 90^\circ$ | $a = 17.409(2) \text{ \AA}$<br>$\alpha = 90^\circ$<br>$b = 4.9166(7) \text{ \AA}$<br>$\beta = 90^\circ$<br>$c = 19.270(3) \text{ \AA}$<br>$\gamma = 90^\circ$ |
| Volume                            | 1875.6(2) Å <sup>3</sup>  | 1649.4(4) Å <sup>3</sup>  |
| Z, Calculated density             | 4, 1.290 mg/m <sup>3</sup>  | 4, 1.354 mg/m <sup>3</sup>  |
| Crystal size                      | 0.45 × 0.35<br>× 0.15 mm <sup>3</sup>   | 0.3 × 0.3<br>× 0.3 mm <sup>3</sup>  |
| Wavelength                        | 0.71073 Å   | 0.71073 Å   |
| Absorption coefficient            | 0.165 mm <sup>-1</sup>  | 0.181 mm <sup>-1</sup>  |
| Final R indices [ $I > 2\sigma$ ] | $R_1 = 0.0456$<br>$wR_2 = 0.1068$   | $R_1 = 0.0312$<br>$wR_2 = 0.0824$   |
| R indices (all data)              | $R_1 = 0.0666$<br>$wR_2 = 0.1171$   | $R_1 = 0.0351$<br>$wR_2 = 0.0839$   |



**Figure 4** Thermogravimetric analysis of DOPO-TA(—), DPPO-TA(- - -), and DEPP-TA (- · -). Step (DOPO-TA) = -36.2%; step (DPPO-TA) = -37.3%.

and DPPO a phosphine oxide. After the addition to *p*-tolylaldehyde the phosphorus atom is covalently bound to the former carbonyl carbon atom in both cases. This leads to the formation of a hydroxyl group. There is no significant difference in the bond lengths of the two compounds (Figs. 2 and 3). The only significant difference is the position of the planes of the toluene ring and of the backbone of the phosphacyclic compound. In the DOPO-TA molecule, these two planes are parallel, while these two parts of the DPPO-TA molecule are out of plane.

Because of the poor solubility of all adducts synthesized with terephthalaldehyde (TDA), it was impossible to obtain them in crystalline form to perform X-ray analysis. Consequently the  $^{31}\text{P}$  NMR data of the TA derivatives had to be compared with the data of the TDA adducts. Studying these data, it became obvious that the  $^{31}\text{P}$  NMR shifts of the synthesized TA adducts are equal to the shifts of the TDA adducts. Hence the reaction of TDA with DOPO, DEPP, and DPPO led to the desired substances. The two phosphorus components were covalently bound to the TDA, leading to new substances with two functional hydroxyl groups. These hydroxyl groups represent two possibilities of linking the substances obtained to the epoxy resin and, hence, these synthesised products (DOPO<sub>2</sub>-TDA, DPPO<sub>2</sub>-TDA, DEPP<sub>2</sub>-TDA) are potentially reactive flame retardants that do not lead to a drastic decrease of the network density after curing the preformulated epoxy resins.

#### Thermal stability of the pure flame retardants

TG analysis of the six adducts was performed, as the reaction of DOPO, DPPO, and DEPP with aldehydes is reversible at elevated temperatures. The initial degradation of the six adducts should be similar. Thermograms of the synthesized substances are shown in Figures 4 and 5. The pyrolysis of DOPO-TA, DPPO-TA, and DEPP-TA starts at about 140°C.

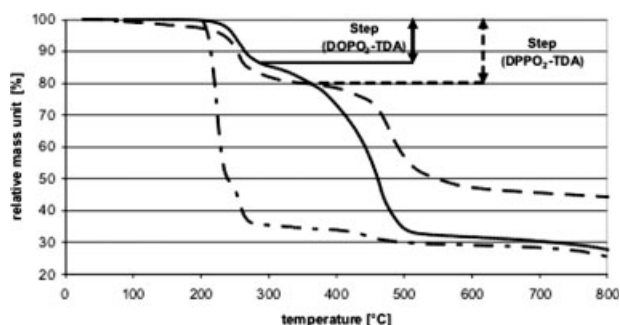
The initial steps of the decomposition are 36 and 37%, respectively. This approximately equals the ratio of tolylaldehyde in DOPO-TA and DPPO-TA. After this, both chemicals decompose in two more steps. DEPP-TA decomposes directly. DOPO<sub>2</sub>-TDA, DPPO<sub>2</sub>-TDA, and DEPP<sub>2</sub>-TDA were analyzed applying this method. The initial decomposition step of DPPO<sub>2</sub>-TDA is 20% which corresponds to molar ratio of terephthalaldehyde. Again the DEPP derivative is pyrolyzed directly. It must be noted that the DPPO derivatives yielded a significantly higher amount of residues than the DOPO and the DEPP derivatives.

#### Thermal stability and burning behavior of preformulations containing bifunctional phosphorus-containing flame retardants

The adducts of DOPO and DPPO with the TDA have a phosphorus content of 10.9 and 10.0%, respectively. DOPO<sub>2</sub>-TDA and DPPO<sub>2</sub>-TDA were bonded covalently to an epoxy novolac (DEN 438) according to Figure 1. The epoxy equivalent weights were titrated. These preformulations were cured as described in the experimental section of this publication.

The burning behavior of all cured epoxy resins was characterised by the standardised UL 94 vertical burning test and the LOI. The virgin DEN 438 cured with both hardeners did not pass the UL 94 classification. The DDM-cured DEN 438 had a LOI of 26.5, while the PACM-cured DEN 438 was burning at an LOI of 22.0. This reflects that the PACM is the hydrogenated analogue of DDM. Consequently, it performed not as well as its aromatic analogue in the burning behaviour tests.<sup>30</sup>

The DDM-cured flame-retardant resin based on DOPO<sub>2</sub>-TDA achieved a V0 rating at a phosphorus content of 1.0%. This sample had an LOI of 29.1. The DPPO<sub>2</sub>-TDA-modified epoxy resin cured with DDM reached the UL 94 V0 rating at a phosphorus content of 1.5%. This polymer had an LOI of 28.9.



**Figure 5** Thermogravimetric analysis of DOPO<sub>2</sub>-TDA (—), DPPO<sub>2</sub>-TDA (- - -), and DEPP-TDA (- · -). Step (DOPO<sub>2</sub>-TDA) = -14.1%; step (DPPO<sub>2</sub>-TDA) = -0.2%.

TABLE II  
UL 94 Rating, LOI, and Glass Transition Temperatures of the DDM- and PACM-Cured  
Flame-Retardant Epoxy Resins Based on DOPO<sub>2</sub>-TDA

| DDM-cured flame-retardant epoxy resins |              |      |   | PACM-cured flame-retardant epoxy resins |              |      |   |
|--|--------------|------|---|---|--------------|------|---|
| Phosphorus content (%P)                | UL 94 rating | LOI  | Glass transition temperature (DSC) (°C) | Phosphorus content (%P)                 | UL 94 rating | LOI  | Glass transition temperature (DSC) (°C) |
| 0.00                                   | not rated    | 26.5 | 218                                     | 0.00                                    | not rated    | 22.0 | 203                                     |
| 0.38                                   | not rated    | 26.9 | 208                                     | 0.38                                    | not rated    | 23.1 | 197                                     |
| 0.60                                   | V1           | 27.5 | 202                                     | 0.59                                    | not rated    | 23.9 | 194                                     |
| 0.82                                   | V1           | 28.4 | 199                                     | 0.82                                    | not rated    | 25.5 | 192                                     |
| 1.02                                   | V0           | 29.1 | 189                                     | 1.01                                    | V1           | 27.6 | 184                                     |
| 1.24                                   | V0           | 30.4 | 181                                     | 1.23                                    | V1           | 28.1 | 179                                     |
| 1.45                                   | V0           | 31.3 | 177                                     | 1.44                                    | V0           | 29.5 | 172                                     |
| 1.69                                   | V0           | 33.1 | 174                                     | 1.68                                    | V0           | 30.2 | 163                                     |

The PACM-cured prepolymers based on DOPO<sub>2</sub>-TDA and DEN 438 qualified for the UL 94 V0 rating at a phosphorus content of 1.4% and had an LOI of 29.5. This is comparable to the DDM-cured epoxies. The DPPO<sub>2</sub>-TDA-modified epoxy resin cured with the same hardener needed 1.7% phosphorus for the same rating and had an LOI of 27.2.

The samples based on DEPP<sub>2</sub>-TDA did not achieve any UL 94 V rating with the processable phosphorus concentrations and the LOI was lower than the LOI of the virgin DEN 438 samples.

It can be summarized that DOPO<sub>2</sub>-TDA and DPPO<sub>2</sub>-TDA performed similar as flame retardants, while the DEPP<sub>2</sub>-TDA at this content had no effect on the flame retardancy of the epoxy resin materials (Tables II-IV).

The decomposition of the resulting thermosets was also investigated by thermogravimetric analysis. The char yields at 800°C are summarised in Table V. Pyrolysis of DDM-cured virgin DEN 438 resulted in a char yield (at 800°C) of 1.5% in normal air and 26.9% under nitrogen. The modification of DEN 438 with the phosphorus compounds reached a higher char yield after curing with DDM. The DDM-cured preformulations containing DOPO<sub>2</sub>-TDA as a flame-retardant and a phosphorus content of 1% had

a char yield of 29.8% under nitrogen and 2.2% in air. The corresponding polymer modified with DPPO<sub>2</sub>-TDA (1% P) yielded 38.1% char under nitrogen and 5.4% in air at 800°C, while the DEPP<sub>2</sub>-TDA-modified polymer with the same phosphorus content gave 45.8% char under nitrogen and 7.6% in air.

The PACM-cured DEN 438 had a char yield of 21.6% under nitrogen and 1.0% in air. This value under nitrogen is 5.3% points lower than that of the DDM-cured DEN 438. This reflects the aliphatic character of the PACM-cured polymer. The PACM-cured preformulation based on DEN 438 and DOPO<sub>2</sub>-TDA yielded a char amount of 26.2% after pyrolysis up to 800°C under nitrogen (0.9% under air). DPPO<sub>2</sub>-TDA-containing samples led to a char yield of 29.6% under nitrogen and 6.1% in air. The corresponding polymer with DEPP<sub>2</sub>-TDA in its polymer backbone (1% P) yielded 32.0% char under nitrogen and 6.7% in air.

When comparing these results, it must be noted that all phosphorus-containing samples after pyrolysis yielded a higher amount of char than the pure resin. Considering the flame-retardant efficiency of the substances used, it is impossible to identify a correlation between the amount of residue formed and the flame retardant-effect of these compounds.

TABLE III  
UL 94 Rating, LOI, and Glass Transition Temperatures of the DDM- and PACM-Cured  
Flame-Retardant Epoxy Resins Based on DPPO<sub>2</sub>-TDA

| DDM-cured flame-retardant epoxy resins |              |      |   | PACM-cured flame-retardant epoxy resins |              |      |   |
|--|--------------|------|---|---|--------------|------|---|
| Phosphorus content (%P)                | UL 94 rating | LOI  | Glass transition temperature (DSC) (°C) | Phosphorus content (%P)                 | UL 94 rating | LOI  | Glass transition temperature (DSC) (°C) |
| 0.00                                   | not rated    | 26.5 | 218                                     | 0.00                                    | not rated    | 22.0 | 203                                     |
| 0.38                                   | not rated    | 26.9 | 205                                     | 0.38                                    | not rated    | 22.9 | 199                                     |
| 0.60                                   | not rated    | 27.4 | 203                                     | 0.60                                    | not rated    | 24.3 | 197                                     |
| 0.82                                   | not rated    | 27.8 | 195                                     | 0.82                                    | not rated    | 25.2 | 194                                     |
| 1.02                                   | not rated    | 28.1 | 193                                     | 1.02                                    | not rated    | 26.0 | 189                                     |
| 1.23                                   | V1           | 28.4 | 189                                     | 1.24                                    | not rated    | 26.8 | 184                                     |
| 1.45                                   | V0           | 28.9 | 185                                     | 1.45                                    | not rated    | 26.9 | 176                                     |
| 1.68                                   | V0           | 29.2 | 167                                     | 1.69                                    | V0           | 27.2 | 161                                     |

TABLE IV  
UL 94 Rating, LOI, and Glass Transition Temperatures of the DDM- and PACM-Cured  
Flame-Retardant Epoxy Resins Based on DEPP<sub>2</sub>-TDA

| DDM-cured flame-retardant epoxy resins |              |      |   | PACM-cured flame-retardant epoxy resins |              |      |   |
|--|--------------|------|---|---|--------------|------|---|
| Phosphorus content (%P)                | UL 94 rating | LOI  | Glass transition temperature (DSC) (°C) | Phosphorus content (%P)                 | UL 94 rating | LOI  | Glass transition temperature (DSC) (°C) |
| 0.00                                   | not rated    | 26.5 | 218                                     | 0.00                                    | not rated    | 22.0 | 203                                     |
| 0.38                                   | not rated    | 26.3 | –                                       | 0.38                                    | not rated    | 21.4 | 197                                     |
| 0.60                                   | not rated    | 25.7 | –                                       | 0.60                                    | not rated    | 20.7 | –                                       |
| 0.82                                   | not rated    | 25.6 | 191                                     | 0.82                                    | not rated    | 20.5 | 189                                     |
| 1.02                                   | not rated    | 25.4 | –                                       | 1.02                                    | not rated    | 20.1 | 186                                     |
| 1.23                                   | not rated    | 24.8 | 186                                     | 1.24                                    | not rated    | 19.8 | 182                                     |
| 1.45                                   | not rated    | 24.9 | 174                                     | 1.45                                    | not rated    | 19.4 | –                                       |
| 1.68                                   | not rated    | 25.7 | 168                                     | 1.69                                    | not rated    | 19.3 | 171                                     |

The DEPP<sub>2</sub>-TDA samples formed the highest amount of char, but no flame-retardant effect was observed in the UL 94 test and the LOI measured at the phosphorus concentrations studied. On the other hand, the DOPO<sub>2</sub>-TDA samples exhibited only slight tendencies of charring. DPPO<sub>2</sub>-TDA exhibited a slightly higher tendency of forming char. But both epoxy material based on the phosphacyclic compounds showed a good performance in the burning tests. These results lead to the conclusion, that all presented phosphacyclic compounds act mainly via a gas phase mechanism.

The flame-retardant samples were also subjected to TD-MS (Fig. 6) to obtain a better insight in the capability of the flame-retardant materials used to form phosphorus-containing volatiles.

For the DOPO- and DPPO- containing samples, TD-MS reveals the formation of PO radicals, whereas the intensity of the PO signal for the DEPP-containing sample is in the range of the virgin epoxy resin.

These results obtained with respect to charring during pyrolysis and the TG-MS investigations correspond quite well with the mechanistic conceptions of phosphacyclic flame retardants presented earlier.<sup>11</sup>

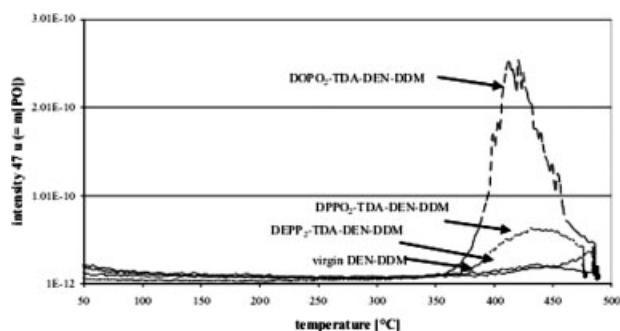
The glass transition temperatures ( $T_g$ ) of all cured epoxy resins were determined by DSC measurements. The virgin DEN 438 cured with DDM had a  $T_g$  of 218°C and of 203°C, if cured with PACM.

Every flame-retardant molecule connected two epoxy novolac molecules in the preformulation reaction. This led to a decreasing number of epoxy groups, while the flame retardant content increased (Fig. 1). The consequence was an increase of the epoxy equivalent number (defined as the mass per equivalent oxirane). The cross-linking density significantly depended on the concentration of epoxy groups. The sample with the highest cross-linking 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 cross-linking density and, hence, to a decreasing  $T_g$ . It must be noted that the decrease of  $T_g$  is quite linear to the phosphorus content of the flame-retardant epoxy resins in these cases (Tables III and IV). Therefore, low flame retardant contents which satisfy the requirements of standardized tests, such as the UL 94 test, are preferable to achieve high glass transition temperatures.

The DDM-cured flame-retardant epoxy resins containing DOPO<sub>2</sub>-TDA and DPPO<sub>2</sub>-TDA had a  $T_g$  of nearly 190°C at the UL 94 V0 rating. The PACM-cured prepolymers reached  $T_g$ 's of 172°C (DOPO<sub>2</sub>-TDA) and 161°C (DPPO<sub>2</sub>-TDA), respectively. These decreases of the  $T_g$ 's considering the loading of flame retardant are comparatively moderate, because the presented flame retardant molecules react with

TABLE V  
Char Yields of the DDM- and PACM-Cured Samples at 800°C

|                          |            |                                 |                                 |                                 |
|--------------------------|------------|---------------------------------|---------------------------------|---------------------------------|
| DDM-cured epoxy novolac  |            |                                 |                                 |                                 |
| Char yield               | Unmodified | DOPO <sub>2</sub> -TDA-modified | DPPO <sub>2</sub> -TDA-modified | DEPP <sub>2</sub> -TDA-modified |
| Under nitrogen           | 26.9%      | 29.8%                           | 38.1%                           | 45.8%                           |
| Under air                | 1.5%       | 2.2%                            | 5.4%                            | 7.6%                            |
| PACM-cured epoxy novolac |            |                                 |                                 |                                 |
| Char yield               | unmodified | DOPO <sub>2</sub> -TDA-modified | DPPO <sub>2</sub> -TDA-modified | DEPP <sub>2</sub> -TDA-modified |
| Under nitrogen           | 21.6%      | 26.2%                           | 29.6%                           | 32.0%                           |
| Under air                | 1.0%       | 0.9%                            | 6.1%                            | 6.7%                            |



**Figure 6** Thermal desorption mass spectroscopy of the epoxy samples.

two functional groups form a better network in the epoxy resin.

### SUMMARY

A novel way of modifying epoxy resins was introduced. Two novel flame retardants based on TDA, DOPO, and DPPO as flame retardants were synthesized. Their structures were verified by NMR analysis and XRD analysis of two similar exemplary molecules (DOPO-TA and DPPO-TA). The novel flame retardants were incorporated successfully in an epoxy novolac resin to form prepolymers. The resultant flame-retardant epoxy resins were cured with DDM and PACM. Depending on the hardener used, the polymers obtained qualified for the UL 94 V0 rating at low phosphorus contents of 1.0 to 1.7% phosphorus with an LOI of up to 33. Applying this method, components with glass transition temperatures of up to 189°C were obtained. The char-forming abilities of the phosphacyclic modified epoxies were compared with those of samples based on the inefficient DEPP. TD-MS was performed for the thermosets. PO radicals could be detected in the case of the DOPO- and DPPO-containing samples. Based on the promising results presented, it may be expected that these bifunctional TDA adducts may be an alternative to the well-described benzoquinone adduct of DOPO.<sup>31–39</sup> The supply of hardeners by Air Products GmbH was highly appreciated. The authors would also like to thank Mrs. Renate Will and Mrs. Marion Lenzner for the DSC and TGA measurements.

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