Preparation and characterization of flame retardant epoxy resins based on phosphorus-containing biphenyl-type phenolic resin

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Abstract: A phosphorus-containing biphenyl-type phenolic resin (PBP) was prepared by dehydration polycondensation of the DOPO-disubstituted 4,4’-biphenyldimethanol compound (BDCA-2DOPO) with phenol in the presence of strong Lewis acid, in which BDCA-2DOPO was prepared by the reaction of DOPO with 4,4’-biphenyldicarboxaldehyde. The PBP resin has been evaluated as the curing agent of o-cresol epoxy resins. Experimental results indicated that the PBP-cured epoxy resins exhibited good thermal stability, high char yields at 700 °C and outstanding flame retardant properties. UL 94 V-0 classifications could be obtained when the phosphorus loading in the epoxy resin is higher than 1.8 wt%.

Introduction

Epoxy resins have been widely used as microelectronics packaging materials due to their many attractive features such as excellent mechanical properties, good chemical and moisture resistance, long-term service time, low-cost and easy processing, etc. [1-2] However, epoxy resins usually contain multi-brominated flame retardants to ensure the materials with the required fire safety. In recent years, the big concerns on environmental problems caused by the toxic substances generated in combustion of multi-brominated flame retardants make the development of halogen-free flame retardant epoxy resins being one of the hot research fields. [3] Hence, many efforts have been made to develop epoxy resins with specially designed chemical structures. It was found that multiaromatic-contained epoxy resins exhibited outstanding flame retardant properties. [4-7] For instance, the epoxy moulding compound derived from biphenyl-type epoxy resins and biphenyl-type novolac resin as curing agent showed the intrinsic flame retardant properties with UL 94 V-0 grade [8, 9].

Phosphorus-contained organic compounds or resins have been known as effective flame retardants for epoxy resins and other polymer materials due to their several advantage features such as high flame-retardant efficiency, low production of corrosive and toxic gases in flames, as well as less harmful to the earth’s environment etc., showing noteworthy potential benefits to replace the commercial multi-brominated flame retardants [10]. In recent years, many kinds of phosphorus-contained organic compounds or resins have been synthesized and evaluated as flame retardants for epoxy resins. [11-15] A phosphorus-contained organic compound, 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO), has
attracted intensive attention due to its high flame retarding efficiency. Hence, a lot of DOPO-added epoxy resins, curing agents or additives have been reported [16-20]. It was found that the thermal decomposition of the DOPO-contained polymers could catalyze the chain transfer of carbonization to form thermal-resistant char layer, which could prevent the heat transfer and inhibit the release of combustible gases.

In this work, a phosphorus-contained biphenyl-type phenolic resin (PBP) was prepared by dehydration polycondensation of a DOPO-disubstituted 4,4'-biphenyldimethanol compound (BDCA-2DOPO) with phenol, in which the BDCA-2DOPO was prepared by the reaction of DOPO with 4,4'-biphenylidicarboxaldehyde. The PBP resin has been evaluated as the curing agent of o-cresol epoxy resins. The thermal properties, degradation behaviours, electrical insulation properties and flame retardant properties of the PBP-cured epoxy resins have been systematically investigated.

Results and Discussion

Synthesis of BDCA-2DOPO and PBP

The phosphorus-contained biphenyl phenolic resin (PBP) was prepared by a two-step procedure (Scheme 1), in which the DOPO-disubstituted 4,4'-biphenyldimethanol (BDCA-2DOPO) was first synthesized by the addition reaction of the $\text{P(O)}-\text{H}$ group in DOPO molecule with the $\text{C(O)}-\text{H}$ group in 4,4'-biphenylidicarboxaldehyde (BDCA) using DMAC as solvent at elevated temperature (120 °C) [21-23]. The dehydration polycondensation of BDCA-2DOPO with phenol catalyzed by $p$-toluenesulfonic acid using NMP as solvent at 120 °C yield the DOPO-substituted phenolic resin (PBP).

Scheme 1. Synthesis of the phosphorus-contained biphenyl resin.

Fig. 1 compares FT-IR spectra of PBP resin with the starting material (DOPO) and the intermediate (BDCA-2DOPO). It can be seen that the disappearance of the absorption peaks at 2385 cm$^{-1}$ (P–H) and the appearance of the absorption peaks at 3239 cm$^{-1}$ (CH–OH) were attributed to the addition reaction of $\text{P(O)}$–H group in
DOPO with the –HC=O group in BDCA. Characteristic absorption peaks at 921 cm\(^{-1}\) (P–O–Ph), 1206 cm\(^{-1}\) (P=O), 1594 cm\(^{-1}\) (P–Ph) were observed in the BDCA-2DOPO, indicating that the cyclic DOPO structure in PBP resin was produced. Fig. 2 compares \(^1\)H NMR spectra of PBP resin and BDCA-2DOPO. It can be seen that the absorption peaks at \(\delta = 5.21-5.44 \text{ ppm } [P–C(OH)–H]\) and \(\delta = 6.47-6.51 \text{ ppm } [P–C(H)–OH]\) in BDCA-2DOPO completely disappeared in PBP resin.

**Fig. 1.** FT-IR spectra of PBP, BDCA-2DOPO and DOPO.

**Fig. 2.** \(^1\)H NMR spectra of PBP and BDCA-2DOPO.
Fig. 3 shows $^{31}$P NMR spectra of PBP resin compared with BDCA-2DOPO, in which the single peaks at $\delta$=33.45 ppm indicated that the dehydration reaction between phenol and BDCA-2DOPO was completed.

The average molecular weight of PBP resin was determined as 2911 g/mol by gel permeation chromatography, and the -OH functionality of PBP resin was calculated as 3.7 [24].

![BDCA-2DOPO and PBP NMR spectra](image)

**Fig. 3.** $^{31}$P NMR spectra of PBP resin and BDCA-2DOPO.

**Thermal and electrical properties of cured epoxy resins**

The DOPO-substituted biphenyl phenolic resin (PBP) was employed as the curing agent of epoxy resins. To evaluate its application potential in microelectronics packaging materials such as Epoxy Moulding Compounds (EMC), the commercial available EMC resin containing o-cresol novolac epoxy resin (CNE) and phenol novolac (PN) have been selected. Tab. 1 shows the chemical compositions of the epoxy resin samples with phosphorus loadings in the range of 0-2.3 wt%.

**Tab. 1.** Chemical compositions of the epoxy resin samples.

<table>
<thead>
<tr>
<th>Samples</th>
<th>CNE wt%</th>
<th>PN wt%</th>
<th>PBP wt%</th>
<th>P wt%</th>
</tr>
</thead>
<tbody>
<tr>
<td>EP-0</td>
<td>65</td>
<td>35</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>EP-1</td>
<td>60.4</td>
<td>30.9</td>
<td>8.7</td>
<td>0.7</td>
</tr>
<tr>
<td>EP-2</td>
<td>56.4</td>
<td>27.3</td>
<td>16.3</td>
<td>1.3</td>
</tr>
<tr>
<td>EP-3</td>
<td>52.9</td>
<td>24.2</td>
<td>22.9</td>
<td>1.8</td>
</tr>
<tr>
<td>EP-4</td>
<td>49.8</td>
<td>21.5</td>
<td>28.7</td>
<td>2.3</td>
</tr>
</tbody>
</table>

Fig. 4 depicts DMA curves of the cured epoxy resins with different phosphorus loadings and Tab. 2 summarizes the thermal and electrical property data. It can be seen that the thermal mechanical property such as the onset temperatures of the storage modulus curves ($T_{onset}$) and the $T_g$ values (defined as the peaks of the tan $\delta$ curves) were decreased with increasing the phosphorus loadings. For instance, the thermally cured EP-4 (P wt% = 2.3) showed $T_g$ of 142.8 $^\circ$C, 15.8 $^\circ$C lower than that of EP-1 (P wt% = 0.7) and 42.1 $^\circ$C lower than that of EP-0 (P wt% = 0), respectively.
addition, the $T_{onset}$ values of EP-4 was 125.0 °C, 3.1 °C lower than that of EP-3 (128.1 °C) and 38.5 °C lower than that of EP-0 (163.5 °C), respectively. According to the rubber theory [25], the relative crosslinking density of cured epoxy resin could be estimated by the storage modulus ratios at the temperature of 40 °C higher than $T_g$. For instance, the storage modulus value of EP-4 at $(T_g+40)$ °C is measured as 16 MPa, which is 46 MPa lower than that of EP-0 (62 MPa), implying that the relative crosslinking density of EP-4 is only 26% compared with EP-0. The bulky DOPO groups in the resin backbone might attribute to the decrease in resin’s crosslinking density, thereby reducing the resin’s $T_g$s.

![DMA curves of cured epoxy resins with different phosphorus loadings.](image)

The volume resistivity ($\rho_v$) and surface resistivity ($\rho_s$) of the thermally cured epoxy resins were measured in the range of $1.2-3.6 \times 10^{15} \Omega \cdot \text{cm}$ and $1.7-3.5 \times 10^{16} \Omega$, respectively (Table 2), demonstrating good electric insulation properties.

### Tab. 2. Thermal and electrical insulating properties of cured epoxy resins.

<table>
<thead>
<tr>
<th>Samples</th>
<th>$T_{onset}$ (°C)</th>
<th>$T_g$ (°C)</th>
<th>$G'$ (50 °C) (GPa)</th>
<th>$G'$ $(T_g+40)$ (MPa)</th>
<th>$\rho_v$ (Ωcm)</th>
<th>$\rho_s$ (Ω)</th>
</tr>
</thead>
<tbody>
<tr>
<td>EP-0</td>
<td>163.5</td>
<td>184.9</td>
<td>2.4</td>
<td>62</td>
<td>$1.7 \times 10^{15}$</td>
<td>$1.9 \times 10^{16}$</td>
</tr>
<tr>
<td>EP-1</td>
<td>140.5</td>
<td>158.6</td>
<td>2.6</td>
<td>39</td>
<td>$2.9 \times 10^{15}$</td>
<td>$2.9 \times 10^{16}$</td>
</tr>
<tr>
<td>EP-2</td>
<td>133.2</td>
<td>150.6</td>
<td>2.6</td>
<td>23</td>
<td>$1.2 \times 10^{15}$</td>
<td>$3.5 \times 10^{16}$</td>
</tr>
<tr>
<td>EP-3</td>
<td>128.1</td>
<td>146.2</td>
<td>3.0</td>
<td>18</td>
<td>$3.6 \times 10^{15}$</td>
<td>$1.8 \times 10^{16}$</td>
</tr>
<tr>
<td>EP-4</td>
<td>125.0</td>
<td>142.8</td>
<td>3.1</td>
<td>16</td>
<td>$1.3 \times 10^{15}$</td>
<td>$1.7 \times 10^{16}$</td>
</tr>
</tbody>
</table>

**Decomposition behaviour and thermal stability of the cured epoxy resins**

Fig. 5 depicts TGA curves of cured epoxy resins in nitrogen and Tab. 3 summarizes the degradation data measured in TGA. It can be seen that the cured epoxy resins did not show any original weight loss when the temperature was scanned up to 300 °C; then started a two-stage thermal decomposition for the higher phosphorus-containing epoxy resins (Fig 5) [26-28]. The first-stage decomposition was observed at temperature range of 300-500 °C, in which the weight losses were decreased with...
increasing phosphorus loadings, probably attributed to the evolving of the DOPO groups linked in the resin backbone. For instance, EP-4 which has the highest phosphorus loading showed the lowest weight loss at 500 °C, compared with EP-0 which showed the highest weight loss. The second-stage decomposition was observed at temperature of >550 °C. It can be seen that the thermally cured EP-3 and EP-4 exhibited the best thermal stabilities due to their high phosphorus loadings.

**Fig. 5.** TGA curves of the thermally cured epoxy resins in nitrogen.

**Tab. 3.** Degradation data of cured epoxy resins determined by TGA in N₂.

<table>
<thead>
<tr>
<th>Samples</th>
<th>T₅ (°C)</th>
<th>Tᵣ₁ (°C)</th>
<th>R₁ (%/°C)</th>
<th>Eₐ₁ (kJ/mol)</th>
<th>Tᵣ₂ (°C)</th>
<th>R₂ (%/°C)</th>
<th>Eₐ₂ (kJ/mol)</th>
<th>Char (%)</th>
<th>IPDT (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>EP-0</td>
<td>418.2</td>
<td>433.0</td>
<td>1.38</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>28.4</td>
<td>878.7</td>
</tr>
<tr>
<td>EP-1</td>
<td>397.2</td>
<td>426.7</td>
<td>0.77</td>
<td>42.7</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>43.2</td>
<td>1282.0</td>
</tr>
<tr>
<td>EP-2</td>
<td>381.7</td>
<td>410.5</td>
<td>0.61</td>
<td>33.8</td>
<td>573.8</td>
<td>0.11</td>
<td>7.8</td>
<td>46.6</td>
<td>1417.9</td>
</tr>
<tr>
<td>EP-3</td>
<td>377.2</td>
<td>407.4</td>
<td>0.42</td>
<td>33.3</td>
<td>553.7</td>
<td>0.26</td>
<td>14.3</td>
<td>52.3</td>
<td>1665.2</td>
</tr>
<tr>
<td>EP-4</td>
<td>345.5</td>
<td>392.8</td>
<td>0.22</td>
<td>18.4</td>
<td>539.4</td>
<td>0.44</td>
<td>23.0</td>
<td>53.5</td>
<td>1726.1</td>
</tr>
</tbody>
</table>

Tab. 3 summarizes the thermal and degradation data of the thermally cured epoxy resins in nitrogen. The phosphorus-containing epoxy resins showed the temperatures at 5 wt% of the original weight loss (T₅) in the range of 345.5-397.2 °C, compared with the phosphorus-free sample (EP-0, 418.2 °C). The temperatures of the first-stage maximum weight loss rate (Tᵣ₁) were measured in the range of 392.8-426.7 °C, the first-stage maximum weight loss rate (R₁) changed from 1.38 %/°C for EP-0 to 0.22 %/°C for EP-4 and the Eₐ₁ decreased from 56.4 kJ/mol to 18.4 kJ/mol with increasing of P loadings from 0 to 2.3 wt%. The char at 700 °C increased from 28.4% for EP-0 to 53.5 % for EP-4, indicating that the thermal stabilities were obviously improved by increasing phosphorus loading in the epoxy resins. In comparison, no second-stage thermal decompositions were observed for the low phosphorus-containing epoxy resins (EP-0 and EP-1).

Much complicated thermal decomposition behaviours in air were observed owing to the air oxidation effect (Fig. 6 and Tab. 4). The first-stage decomposition was
observed at temperatures of lower than 400 °C, and the second-stage ones, attributed to the resin backbone decomposition, were measured in the temperature range of 400-550 °C. A third-stage decomposition, which was not detected in nitrogen, was probably due to the char oxidation by air after the second stage decomposition. The weight loss rates at the third-stage were depressed by the incorporation of phosphorus and biphenyl groups. The depression on weight loss rate lowered the release rate of combustible products from the decomposition of epoxy resins, consequently enhancing the resins' flame retardant property.

![Graph showing TGA curves of the thermally cured epoxy resins in air.]

**Fig. 6.** TGA curves of the thermally cured epoxy resins in air.

**Tab. 3.** Degradation data of cured epoxy resins determined by TGA in air.

<table>
<thead>
<tr>
<th>Samples</th>
<th>T_{5} (°C)</th>
<th>T_{R1} (°C)</th>
<th>R_{1} (%)</th>
<th>E_{a1} (kJ/mol)</th>
<th>T_{R2} (°C)</th>
<th>R_{2} (%)</th>
<th>E_{a2} (kJ/mol)</th>
<th>T_{R3} (°C)</th>
<th>R_{3} (%)</th>
<th>E_{a3} (kJ/mol)</th>
<th>Char (%)</th>
<th>IPDT (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>EP-0</td>
<td>413.0</td>
<td>430.9</td>
<td>0.68</td>
<td>56.0</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>613.5</td>
<td>0.54</td>
<td>33.5</td>
<td>0.9</td>
<td>529.8</td>
</tr>
<tr>
<td>EP-1</td>
<td>397.3</td>
<td>417.4</td>
<td>0.81</td>
<td>59.5</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>644.0</td>
<td>0.42</td>
<td>30.3</td>
<td>13.6</td>
<td>669.9</td>
</tr>
<tr>
<td>EP-2</td>
<td>384.6</td>
<td>404.5</td>
<td>0.67</td>
<td>50.3</td>
<td>561.0</td>
<td>0.18</td>
<td>10.8</td>
<td>663.4</td>
<td>0.28</td>
<td>25.1</td>
<td>23.9</td>
<td>812.7</td>
</tr>
<tr>
<td>EP-3</td>
<td>373.3</td>
<td>397.3</td>
<td>0.52</td>
<td>40.8</td>
<td>550.9</td>
<td>0.21</td>
<td>13.2</td>
<td>673.5</td>
<td>0.27</td>
<td>25.8</td>
<td>28.3</td>
<td>894.3</td>
</tr>
<tr>
<td>EP-4</td>
<td>355.0</td>
<td>388.3</td>
<td>0.41</td>
<td>31.1</td>
<td>542.6</td>
<td>0.28</td>
<td>15.2</td>
<td>761.9</td>
<td>0.31</td>
<td>42.2</td>
<td>35.8</td>
<td>1056.2</td>
</tr>
</tbody>
</table>

Horwitz-Metzger Equation was employed to determine the activation energy of the first-stage thermal decomposition for the thermally cured epoxy resins with different phosphorus loadings. Fig. 7 shows plots of the ln{ ln(1-α)-1} versus θ, in which all of the slope data were obtained with good correlation coefficients, higher than 0.99. The activation energy values of the thermal decompositions for the thermally cured epoxy resins are listed in Tab. 3 and 4.

The thermal stabilities of the thermally cured epoxy resins were assessed by two parameters: T_{5} and the integral procedure decomposition temperature (IPDT), in which T_{5} determined the apparent thermal stability of the epoxy resins, i.e., the failure temperatures of the resins in processing, and IPDT exhibited the resin inherent thermal stability, i.e., the decomposition characteristics of the resin volatile composition. In Table 3 and 4, it can be seen that the phosphorus-containing epoxy
resins showed the relatively lower $T_5$ than the phosphorus-free resin, since phosphorus groups would decompose at relative low temperatures. On the other hand, introduction of biphenyl and phosphorus groups into the epoxy resins would significantly increase the IPDT. The highest IPDT of 1726.1 °C was observed for EP-4 in N$_2$, 96.4% increase compared with EP-0, implying obvious improvement in thermal degradation stability [29]. In air, the thermally cured epoxy resins exhibited much lower IPDT values than those in nitrogen. However, impacts of the incorporated phosphorus and biphenyl groups in the epoxy resin backbone are similar to that in N$_2$. It was recognised that the phosphorus-containing groups and the biphenyl segments in the resin backbone could improve the char forming capacity in high yield at high temperatures. Therefore, EP-4 exhibited the highest IPDT (1726.1 °C in N$_2$ and 1056.2 °C in air, respectively) due to its large amounts of phosphorus and biphenyl group loadings [29].

\[ \text{Fig. 7. Typical plots of } \ln\left(\frac{1}{1-\alpha}\right) \text{ versus } (T-T_{\text{max}}) \text{ for the 2}^{\text{nd}} \text{ decomposition of the thermally cured epoxy resin in N}_2. \]

**Flame retardant properties of the cured epoxy resins**

The flame retardant properties of the thermally cured epoxy resins were examined with LOI, UL94 test and cone calorimeter test (Table 5). With increasing of the phosphorus loadings, LOI values of the epoxy resins were significantly increased from 21 to 27 and the total burning time tested by UL 94 method decreased from >250 to 11.1s, indicating that the introduction of phosphorus and biphenyl groups has obvious impacts on improving the resin flame retardant properties. When the phosphorus loading was higher than 1.8 wt% (EP-3 and EP-4), UL 94 V-0 grade was obtained. In comparison, the resins with lower phosphorus loadings (EP-0 and EP-1) exhibited poor flame retardancy.

The cone calorimeter is one of the most effective bench-scale methods to evaluate the flammability properties of polymer materials, in which the total time of ignition (TTI), the heat release rate in the peak (pHRR) and the mass loss rate in the peak (pMLR) are the important parameters to determine the fire resistance [30,31]. Fig. 8 and 9 show the combustion process of the representative epoxy resins (EP-0 and EP-3). Compared with the phosphorus-free epoxy resin (EP-0), the phosphorus-
containing resin (EP-3) showed to some extent the reduced pHRR and pMLR (Table 6). The decrease in the total heat release (THR) was also observed. In addition, the TTI data were measured at 51-52 s. The char formation of the cured epoxy resins was apparently enhanced with the incorporation of DOPO groups in the resin backbone. The char yields increased with increasing of the phosphorus and biphenyl groups in the resins. The char formation could limit the production of combustible gases, reduce the exothermicity of pyrolysis reactions and inhibit the thermal conductivity of the burning materials, thereby improving the flame retardant properties of the resins by the condensed-phase mechanism. [30]

**Tab. 5.** Flame retardant properties of the thermally cured epoxy resins.

<table>
<thead>
<tr>
<th>Samples</th>
<th>LOI</th>
<th>Total burning time (s)</th>
<th>UL94 grade</th>
</tr>
</thead>
<tbody>
<tr>
<td>EP-0</td>
<td>21</td>
<td>&gt;250</td>
<td>Not V-2</td>
</tr>
<tr>
<td>EP-1</td>
<td>23.5</td>
<td>&gt;250</td>
<td>Not V-2</td>
</tr>
<tr>
<td>EP-2</td>
<td>24.5</td>
<td>58.3</td>
<td>V-1</td>
</tr>
<tr>
<td>EP-3</td>
<td>26</td>
<td>15.2</td>
<td>V-0</td>
</tr>
<tr>
<td>EP-4</td>
<td>27</td>
<td>11.1</td>
<td>V-0</td>
</tr>
</tbody>
</table>

**Fig. 8.** Heat release rate plots versus time of EP-0 and EP-3.

**Fig. 9.** Mass loss rate plots versus time of EP-0 and EP-3.
Conclusions

A phosphorus-contained biphenyl-type phenolic resin (PBP) has been prepared, which was confirmed to be an effective curing agent for the commercial o-cresol epoxy resins. The thermally cured epoxy resins exhibited good thermal stability (T$_s$ above 340 °C), high char yields at 700 °C and good flame retardant properties. UL 94 V-0 grade could be obtained if the phosphorus loading in the resin is higher than 1.8 wt%.

Experimental part

Materials

9,10-Dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO) was prepared according to the literature.[19] 4,4'-Biphenyldicarboxaldehyde (BDCA, purchased from Shanghai Jiachen Chemicals, China) was recrystallized from toluene before use. Phenol, sodium bicarbonate and p-toluenesulfonic acid (p-TS) (Beijing Beihua Fine Chemicals, China) were used as received. Toluene (Beijing Beihua Fine Chemicals, China) was refluxed with sodium and distilled before use. N,N-Dimethylacetamide (DMAc) and N-methylpyrrolidinone (NMP) were distilled over P$_2$O$_5$ and then stored with molecular sieves. Triphenylphosphine (TPP, Sinopharm Chemical Reagent Co. China) was used as received. Phenol novolac resin (PN, trade name TD-2131, hydroxyl equivalent 105 g/mol, softening point 80 °C) was purchased from Dainippon Ink & Chemicals Inc., Japan and used as received. o-Cresol novolac epoxy resin (CNE, trade name 195LL, epoxy equivalent 195 g/mol, softening point 70 °C) was purchased from Yuka Shell Epoxy KK, Japan and used as received.

Synthesis of BDCA-2DOPO compound

BDCA (21.0 g, 0.2 mol), DOPO (47.5 g, 0.22 mol), and DMAc (200 mL) were charged into a 500 mL three-necked, round-bottom flask equipped with a mechanical stirrer and a thermometer. The reaction mixture were stirred and heated at 120 °C for 5 hours. During the reaction processing, the reaction mixture became thick due to the precipitation of the reaction product. The filtered precipitant was washed with toluene and dried in vacuum at 150 °C to give a white powder (yield, 99%; melt point, 245 °C). IR (KBr, cm$^{-1}$): 921 (P–O–Ph), 1206 (P=O), 1594 (P–Ph), 3271 (CH–OH). $^1$H NMR (300 MHz, DMSO-$d_6$, ppm): 5.21–5.44 (m, 2H), 6.47–6.51 (m, 2H), 7.15–7.31 (m, 4H), 7.39–7.68 (m, 13H), 7.76–7.82 (m, 2H), 8.00–8.05 (m, 1H), 8.09–8.24 (m, 4H). $^{31}$P NMR (300 MHz, DMSO–$d_6$, ppm): 31.04. Elem. Anal. Calcd. for C$_{38}$H$_{29}$O$_5$P$_2$ (642): C, 71.03%; H, 4.39%. Found: C, 71.03%; H, 4.50%.

Synthesis of the phosphorus-containing biphenyl-type phenolic resin (PBP)

BDCA-2DOPO (103.0 g, 0.16 mol), phenol (60.2 g, 0.64 mol), NMP (2000 mL), and toluene (250 mL) were put into a 2000-mL, three-necked, round-bottom flask

Tab. 6. Cone calorimeter data of the thermally cured epoxy resins.

<table>
<thead>
<tr>
<th>Samples</th>
<th>TTI (s)</th>
<th>pHRR (kW/m$^2$)</th>
<th>THR (MJ/m$^2$)</th>
<th>pMLR (g/s)</th>
<th>Char (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>EP-0</td>
<td>51</td>
<td>754</td>
<td>59.0</td>
<td>0.405</td>
<td>17.6</td>
</tr>
<tr>
<td>EP-3</td>
<td>52</td>
<td>593</td>
<td>51.3</td>
<td>0.335</td>
<td>26.2</td>
</tr>
</tbody>
</table>
equipped with nitrogen inlet, a mechanical stirrer, and a Dean-Stark trap with a condenser and a thermometer. With nitrogen purging, p-TS (2.5 g, 16.0 mmol) was added to the solution. The reactants were heated at 140-150 °C with stirring for 24 hours. The resulted water was removed with distilled toluene, and the distilled toluene was returned to the flask. The resulting mixture was neutralized with 5% sodium bicarbonate solution and then extracted with chloroform. The organic layer was collected and concentrated under a reduced pressure to give a product. The product was dried in vacuum at 160 °C for 48 hours (yield, 70%; softening point, 73 °C). IR (KBr, cm⁻¹): 927 (P–O–Ph), 1205 (P=O), 1604 (P–Ph), 3239 (CH–OH). ¹H NMR (300 MHz, DMSO-d₆, ppm): 5.12–5.18 (m, 2H), 6.67–8.00 (m, 30H). ³¹P NMR (300 MHz, DMSO-d₆, ppm): 33.45.

**Preparation of the PBP-cured epoxy resins**

The cured halogen-free epoxy resins were prepared according to the resin chemical compositions (Tab. 1). The o-cresol novolac epoxy resin was blended with phenol novolac resin and synthesized phosphorus-contained biphenyl-type phenolic (PBP) at 150 °C to give homogeneous solution. TPP as curing catalyst was added with mechanically stirring to ensure the catalyst well dispersed in the resin solution. The epoxy resin samples were thermally cured at 150°C for 3 hours, followed by 180 °C for 2 hours. After post-cured at 200 °C for 1 hour, the cured epoxy resins with different phosphorus loadings were obtained.

**Characterization**

¹H and ³¹P NMR spectra were recorded with a Bruker AVANCE 400 NMR spectrometer at 400 MHz with DMSO-d₆ as a solvent. Fourier transform infrared (FTIR) spectra were obtained with a Perkin-Elmer 782 FTIR instrument. Thermal gravimetric analysis (TGA) and Dynamic mechanical analysis (DMA) were recorded on Perkin-Elmer 7 series thermal analysis system. Gel permeation chromatography (GPC) was carried on Waters 1515 equipped with HR1, HR0.5 Waters Styragel columns, using tetrahydrofuran (THF) as eluent. Flame retardancy of the cured resins was determined by the limited oxygen index (LOI) method specified in ASTM D2893. The UL94 method was also used to evaluate flame retardancy, which was performed on sheets (100×13×3 mm) under the condition of the standard test (ASTM D635-77). Combustion behaviours were investigated by a cone calorimeter (Fire Testing Technology Co.) at heat flux of 50 kW/m².

**Determination of thermal stability parameters**

The initial decomposition temperature (T₅) was determined with the temperature of 5% weight loss of the sample. The maximum weight loss rate (Rₙ) and the temperature at maximum rate of weight loss (Tₙ) were taken from the peak values of differential thermogravimetric (DTG) thermograms. The integral decomposition temperature (IPDT) was calculated from:

\[ IPDT = A'K(T_f - T_i) + T_i \]  

where A' is the area ratio of total experimental curve defined by the total TGA thermogram, K the coefficient of A', T_i the initial experimental temperature, and T_f the final experimental temperature. A representation of S₁, S₂, and S₃ for calculating A' [A' = (S₁+S₂)/(S₁+S₂+S₃)] and K[K = (S₁+S₂)/S₁] is shown in Fig. 11. [27]
Fig. 11. Schematic representation of $S_1$, $S_2$ and $S_3$ for $A^*$ and $K^*$ (EP-0 in nitrogen at a heating rate of 10 °C/min).

Calculation of activation energy of sample decomposition

The activation energy ($E_a$) for the cured epoxy resins’ decomposition was calculated from the TGA thermogram, through the integral method based on the Horwitz-Metzger Equation [27, 32]:

$$\ln[\ln(1-\alpha)^{-1}] = \frac{E_a}{RT_{\text{max}}^2}$$  \hspace{1cm} (2)

where $\alpha$ is the decomposition ratio, $\theta$ the difference between $T$ and $T_{\text{max}}$, $T_{\text{max}}$ the temperature of maximum rate of weight loss, and $R$ the ideal gas constant. The activation energy was given by the straight line corresponding to the plot of $\ln[\ln(1-\alpha)^{-1}]$ versus $\theta$.

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References