Figure 1: (a) The form and synthesis steps of DP. (b) FT-IR spectra of DOPO, PPOA and DP, (c) ^{1}H NMR of DP. (d) ^{31}P NMR of raw materials and DP. (e) high resolution mass spectrometry of DP.
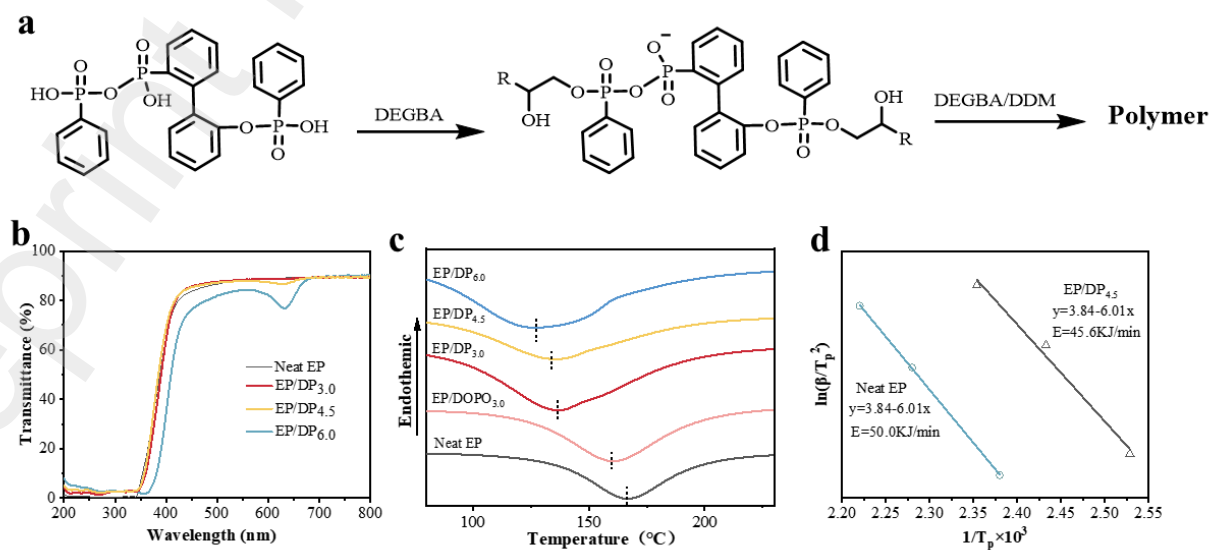
Figure 2. (a) Curing promotion mechanism of DP. (b) Optical performance of EP samples. (c) DSC curves of EP samples at a temperature increase rate of 10 K/min. (d) Kissinger method of fitting curves for EP and EP/DP$_{4.5}$.
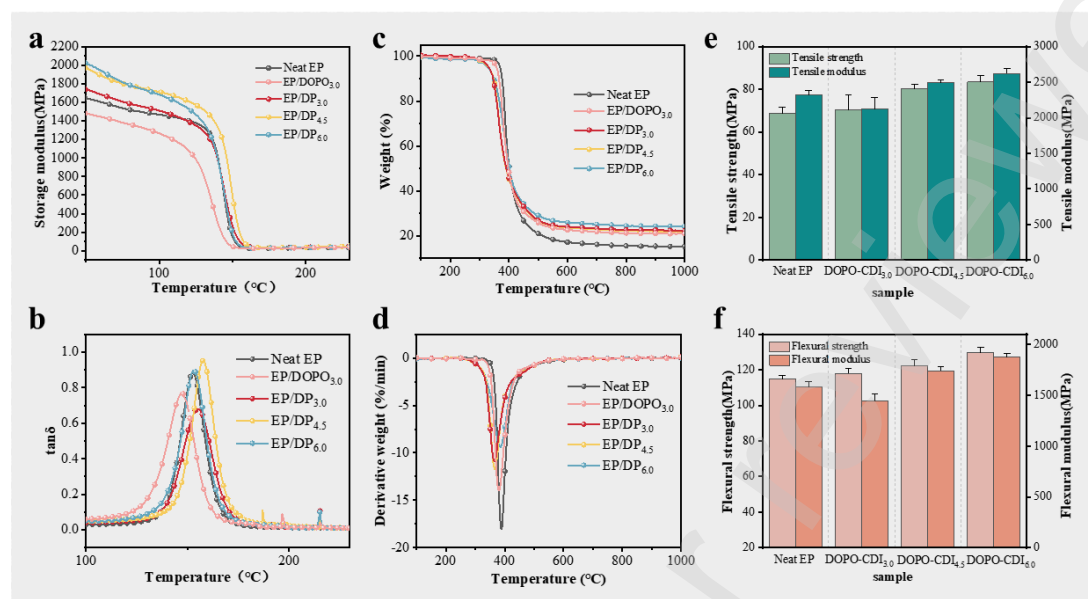

Figure 3. (a) Curves of storage modulus and (b) loss modulus versus temperature. (c) Curves of weight and (d) derivative weight as a function of temperature. (e) Tensile and (f) Flexural Properties of EP Samples.
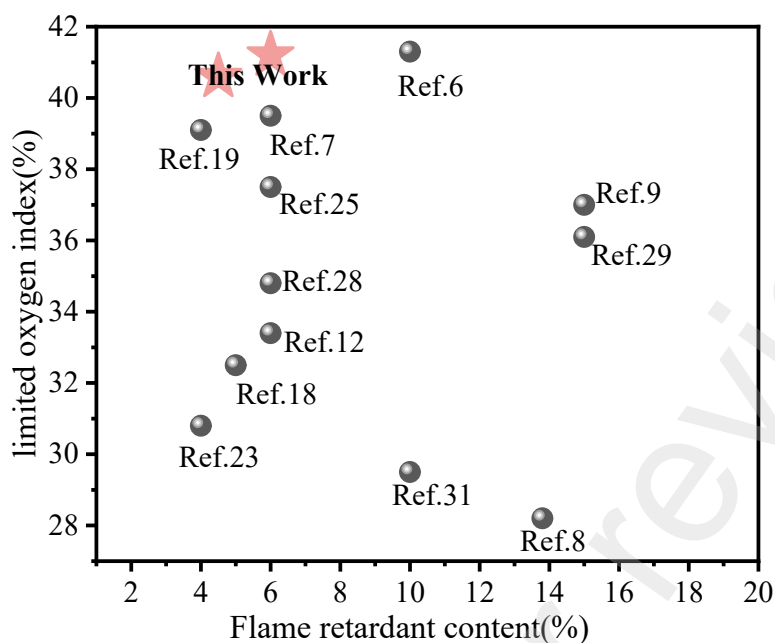
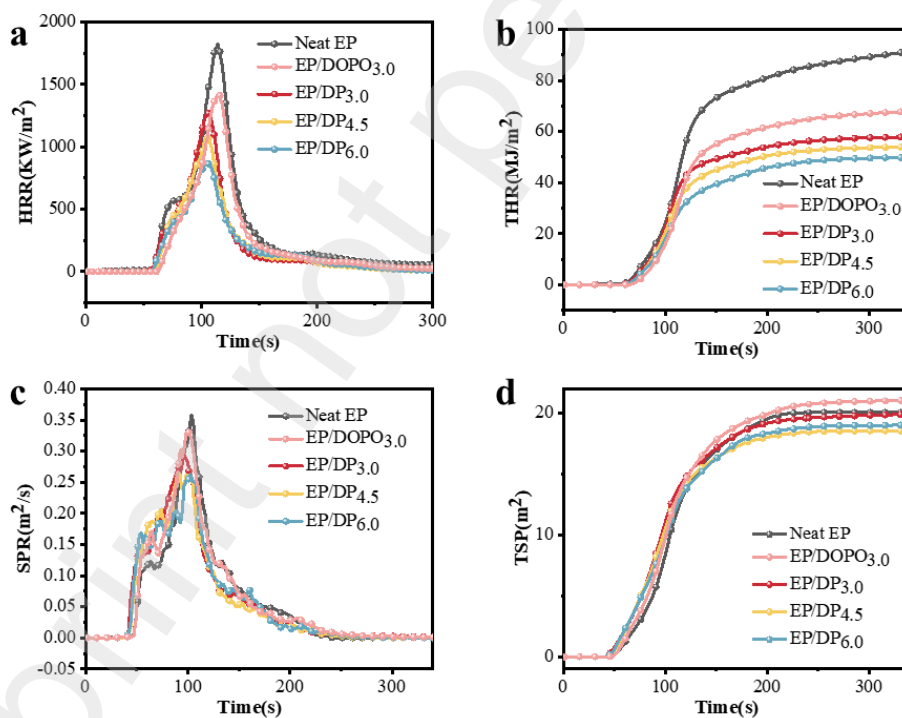**Figure 4**. Scatter Plot of Flame Retardant Efficiency Comparison of Flame Retardants.

Figure 5. (a)HRR. (b)THR. (c)SPR. (d)TSP curves of EP thermosets obtained from cone calorimetry.
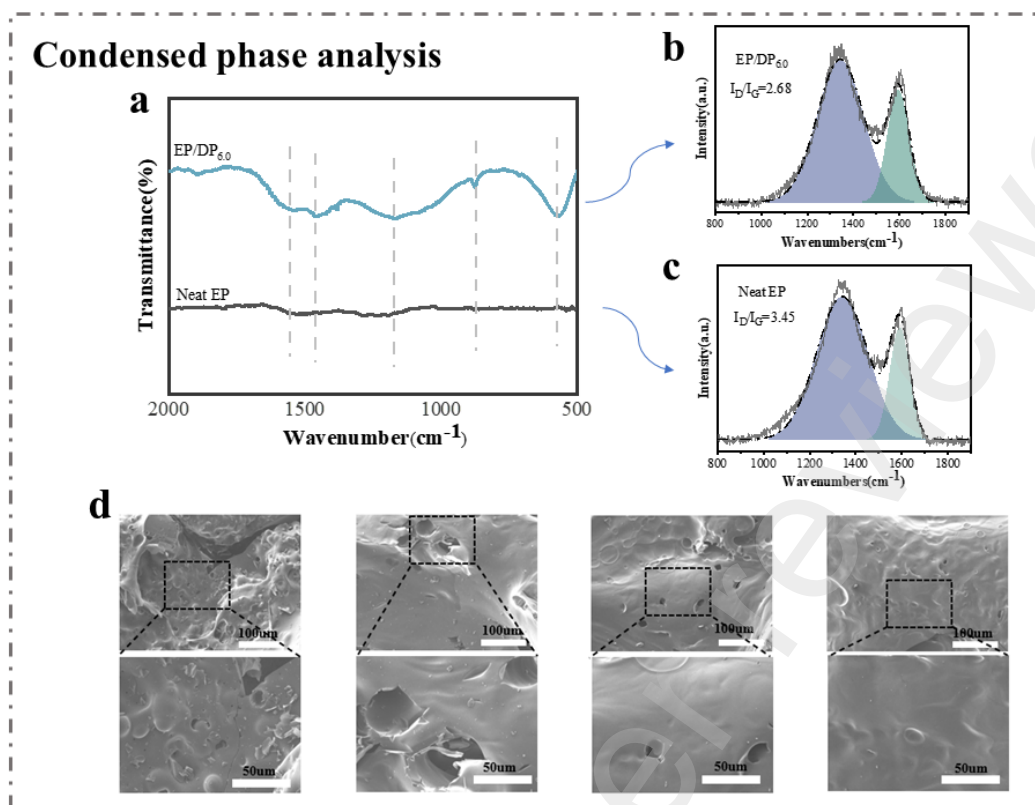
Figure 6. (a) FTIR of EP/DP$_{6.0}$ and Neat EP combustion residues. (b) Raman spectral fitting curve of EP/DP$_{6.0}$ and (c) Neat EP. (d) Microscopic morphology of combustion residues of EP samples (100x and 270x).
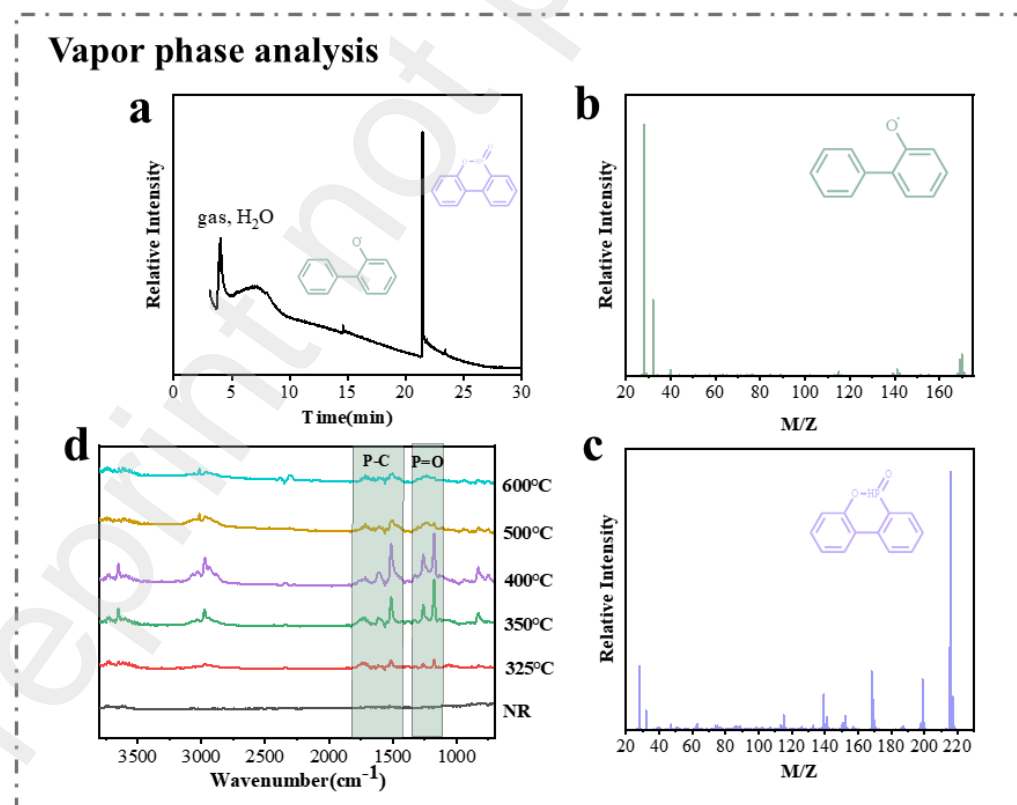
Figure 7. (a)Thermal cleavage Py-GC/MS spectra of DP. (b)Partial radical fragments and (c)DOPO fragments from thermal cleavage. (d)TG-IR spectrum of EP/DP$_{6.0}$.
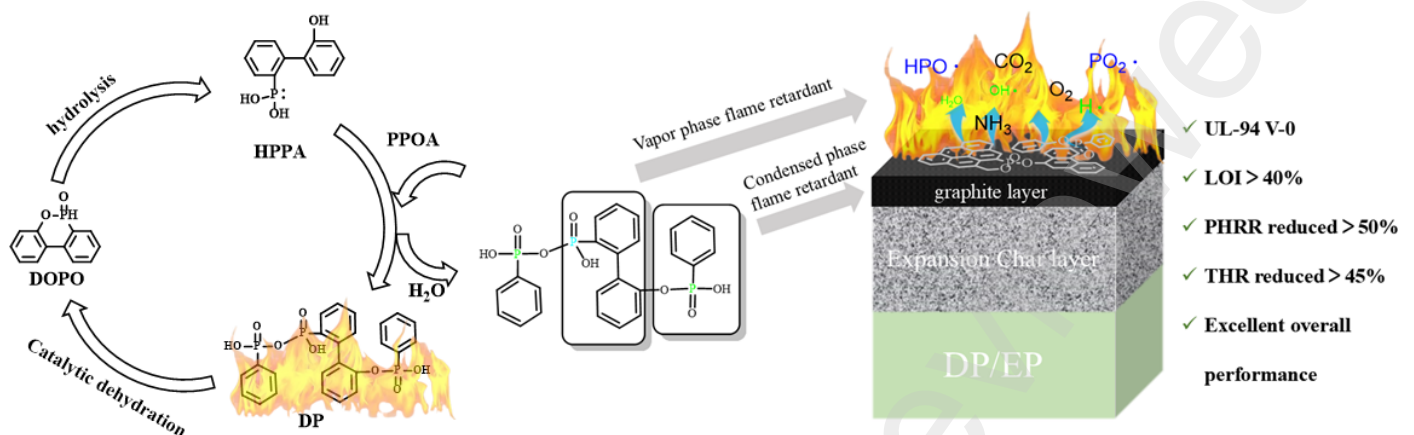
Due to the excellent catalytic charring ability of PPOA, DP is able to re-form DOPO when heated, thus avoiding the adverse effect of DOPO on the material performances while providing the gas-phase flame retardant effect of DOPO.

Figure 8. DP design concept and mechanism of action.

1   **A high-performance flame retardant liquid synthesized on the basis of DOPO**

2   **hydrolysis products avoids the defects of DOPO**

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11   **ABSTRACT:**

12   It was first proposed to use 2-(2-hydroxyphenyl) phenyl phosphonic acid

13   (HPPA), which is hydrolysis product of DOPO, has a structure more similar to EP, to

14   replace DOPO in the preparation of flame retardant, and finally synthesized a highly

15   efficient liquid flame retardant DP based on HPPA, the theoretical phosphorus content

16   of DP is up to 17.5wt%, so EP can achieve excellent flame retardant/inhibit

17   combustion effect with a small amount addition of DP. For example, the LOI of

18   EP/DP$_{6.0}$ is increased to 41.2% and reaches the V-0 rate of UL-94, the PHRR and

19   THR are reduced by 52.4% and 45.2% respectively, in addition, the addition of DP in

20   small quantities does not destroy the overall performance of EP, maintains and

21   improves the excellent mechanical and thermal properties of epoxy resin as a whole,

22   and DP has excellent curing promoting effects, meeting the processing and use

23   requirement of high performance EP. It is better than DOPO overall and has good

24   application prospects.
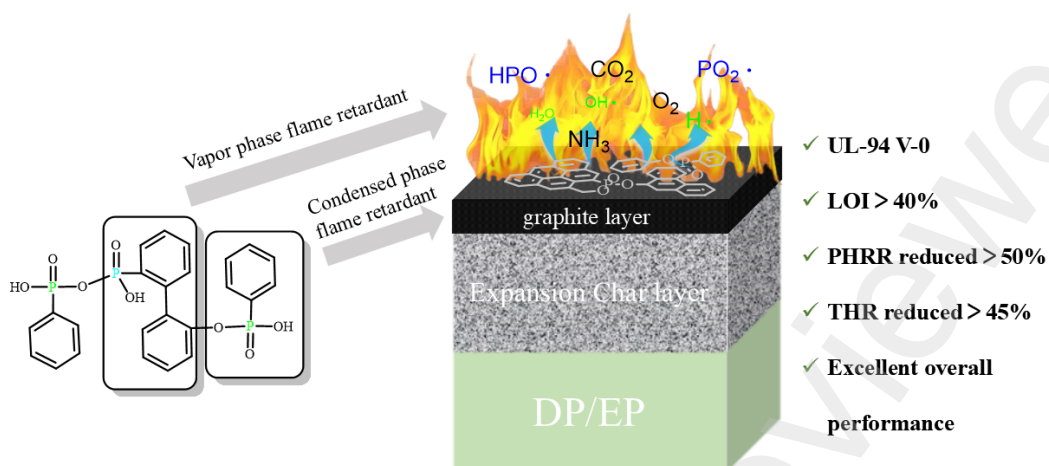
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26   **KEYWORDS**: Epoxy resin, Flame retardant, Overall properties, DOPO, HPPA

2

1. INTRODUCTION

Epoxy(EP) are thermosetting material widely used in many fields and have attracted much attention in recent years due to their high specific strength, excellent thermal stability and outstanding chemical resistance [1][2][3]. However, similar to most organic carbon skeleton materials, epoxy resins are extremely flammable, which greatly restricts the application of epoxy resins, especially in aerospace, railway transportation, electrical and electronic fields that require high safety [4][5]. Therefore, the flame retardant modification of epoxy resins is an important and valuable topic.

The current research on the flame retardant modification of EP mainly focuses on phosphorus flame retardants, which have the advantages of being environmentally friendly, highly effective and strongly active compared to traditional halogen and metal-based flame retardants [6][7], and can be tailored to the functionality of different application requirements [8]. For example, IDPP, a latent curing agent based on 9,10-Dihydro-9-oxa-10-phosphaphenanthrene-10-oxide(DOPO) and imidazole developed by Xu et al. utilizes a coordination effect to reduce imidazole activity, enabling EP to remain processable for a long time at room temperature [9].

DOPO is one of the most commonly used organophosphorus flame retardants, however, unmodified DOPO mainly plays the role of vapor phase flame retardant, so the flame retardant efficiency is poor and often needs to be added in large quantities to the material to achieve a better flame retardant effect [10][11]. According to the experiment, we found that the heterophenanthrene group of DOPO does not bring good thermal stability to the matrix material due to the plasticizing effect, and DOPO is a solid that is difficult to dissolve in the EP monomer, so the processing of DOPO-modified EP is often time consuming and energy wasting [10][12]. In contrast, we believe that 2-(2-hydroxyphenyl) phenyl phosphonic acid(HPPA), a by-product of DOPO synthesis, has a chemical structure similar to that of DEGBA, and therefore may be more suitable as a matrix material for the preparation of EP flame retardants.

3

55   Normally, HPPA is difficult to be separated from the mixture with DOPO,

56   therefore, no research on the modification of HPPA has been conducted in the field of

57   epoxy flame retardant until now, some studies have shown that acidic conditions can

58   promote the conversion of DOPO to HPPA [13].

59   It is well known that the addition of large amounts of flame retardants can lead to

60   the deterioration of the overall performance of the substrate[14][15], so we are devoted

61   to the design of a high-phosphorus content flame retardant based on HPPA, to achieve

62   excellent flame retardancy and good overall performance with a low level of additive.

63   In this work, we utilized the difference of nucleophilicity between the functional

64   group in HPPA and PPOA, and manufactured a liquid flame retardant DP with high

65   phosphorus content by vacuum heating assistance, which can make the epoxy resin

66   system reach 1 wt% phosphorus content by adding only 6 wt%, has both gas-phase and

67   condensed-phase flame retardant effects, which meets our expectation of excellent

68   flame retardancy without destroying the overall properties of EP.

4

2. MATERIALS AND METHODS

2.1. Materials

In supplementary document.

2.2. Synthesis of DP

Firstly, 25.92 g of DOPO (0.12 mol) and 15.8 g of PPOA (0.1 mol) were weighed into a 250 ml three-necked flask equipped with magnetic stirring and condensation reflux device. Measure 100 ml of DMF and 25 ml of dilute hydrochloric acid (1mol/L) with a measuring cylinder and slowly drop the dilute hydrochloric acid into DMF, and then add it to the three-necked flask after mixing well and stirring at 100°C for 8h to activation. After that, the system was transferred to a vacuum reaction device and reacted at -80 Kpa and 90 °C for 2 h. Finally, all the water and most of the DMF were removed by rotary evaporation then washed 3 times with toluene to remove the residual DMF and excess DOPO to obtain a colorless and transparent liquid flame retardant DP.

2.3. Fabrication of EP thermosets

In the preparation of EP/DP, a specific amount of EP monomer and DP were weighed and mechanically stirred at 90°C for at least 10 min to obtain a homogeneous solution, and then DDM was added after the system cooled down to 80°C. After completely dissolved, put into the vacuum defoamer to remove the foam and pour into the mold that has been preheated then put into the oven. Curing program is set to 80°C 1h, 130°C 2h, 180°C 2h.

Neat EP and EP/DOPO3.0 were prepared in a similar procedure by adding DDM after obtaining a homogeneous system at 100°C, dissolving, defoaming and placing in an oven, and the curing procedure followed the typical Neat EP curing steps of 100°C for 2h, 150°C for 2h, and post-curing at 180°C for 2h. Detailed formulations of each group of thermosetting resins are shown in Table 1.

Table 1. The formulations of epoxy thermosets

5

Sample	DGEBA(wt%)	DDM(wt%)	DP(wt%)	P(wt%)
Neat EP	80	20	0	0
EP/DOPO$_{3.0}$	77.6	19.4	3.0	0.43
EP/DP$_{3.0}$	77.6	19.4	3.0	0.53
EP/DP$_{4.5}$	76.4	19.1	4.5	0.79
EP/DP$_{6.0}$	75.2	18.8	6.0	1.05

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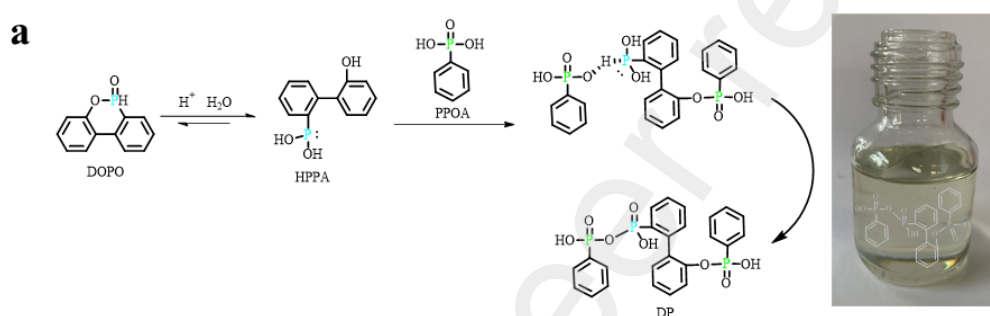
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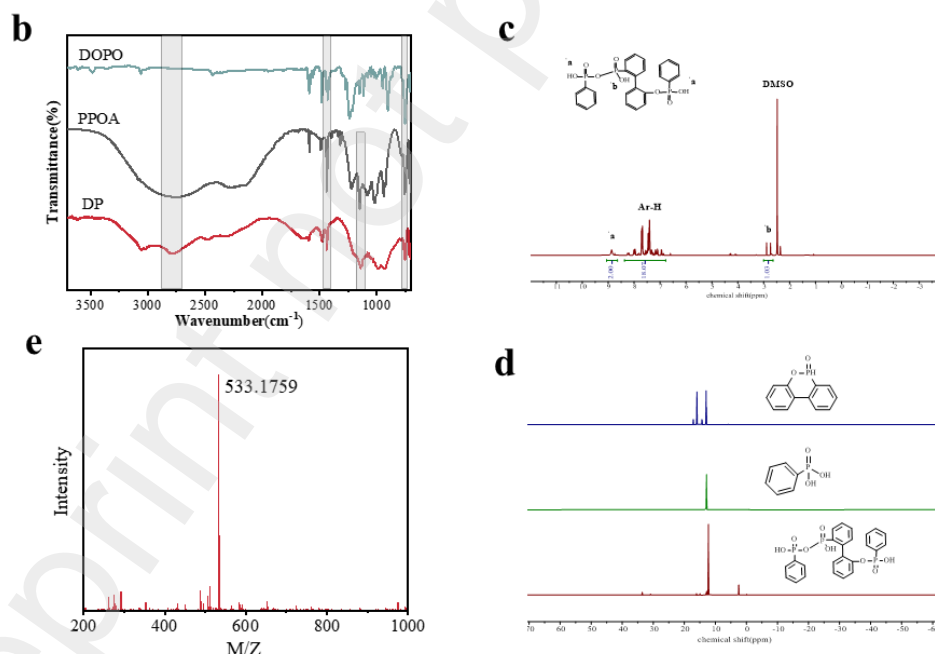
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Figure 1: (a) The form and synthesis steps of DP. (b) FT-IR spectra of DOPO, PPOA and DP, (c) ^{1}H NMR of DP. (d) ^{31}P NMR of raw materials and DP. (e) high resolution mass spectrometry of DP.

6

102   **2.4. Characterizations**

103   In supplementary document.

7

3. RESULTS AND DISCUSSION

3.1. Characterization of DP

We have accurately characterized DP by FTIR, 1H NMR, 31P NMR and high-resolution mass spectrometry as shown in Fig. 1, firstly, the wavelength 2820 cm^{-1} reflects the P-OH bond absorption peaks of HPPA and PPOA**Error! Reference source not found.**[16][18]. The absorption peak at 1440 cm^{-1} reflects the P-Ph absorption peak of DP liquid, while the P=O absorption peak of DP is similar to that of PPOA located at 1140 cm^{-1}[20][21].

^{1}H NMR and ^{31}P NMR were used to characterize the chemical environments of the atoms within the DP molecule and the areas of the peaks corresponded to the structural formulae of DP. In the ^{31}P NMR spectrum, only one absorption peak appears due to the similarity of the chemical environment in which each phosphorus atom in the DP molecule. Multiple peak analyses were reported as follows: ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.81 (d, J = 58.9 Hz, 2H), 8.37 – 6.78 (m, 18H), 3.00 – 2.64 (m, 1H). 31P NMR (202 MHz, DMSO-d6) δ 12.24. It is worth noting that trace PPOA may form coordination products with H_2O, but this does not affect the excellent overall performance of DP.

In order to further demonstrate the correctness of our analysis of the FTIR and NMR spectra, we took the DMF solution of DP and carried out high resolution mass spectrometry, which showed that the molecular weight results of DP corresponded to its structural formula, thus proving the successful synthesis of DP.

3.2. Optical performance

Since DP liquid has good compatibility with the matrix materials, its introduction does not significantly reduce the transparency of the EP, and the maximum visible light transmission is higher than 90%, as observed in Fig 2b. at low DP addition levels. However, when the addition amount reaches 6 wt%, the overall transmittance decreases and is accompanied by the greenish phenomenon, which may be due to the

8

131   participation of DP in the curing reaction that affects the crosslinking network

132   structure of EP to a relatively large extent. In addition, the material exhibits excellent

133   overall UV shielding due to the fact that the aromatic structure promotes the

134   absorption of UV light by EP[22][23], an advantage that makes EP/DP a potential

135   candidate for use in electronic packaging applications[24].
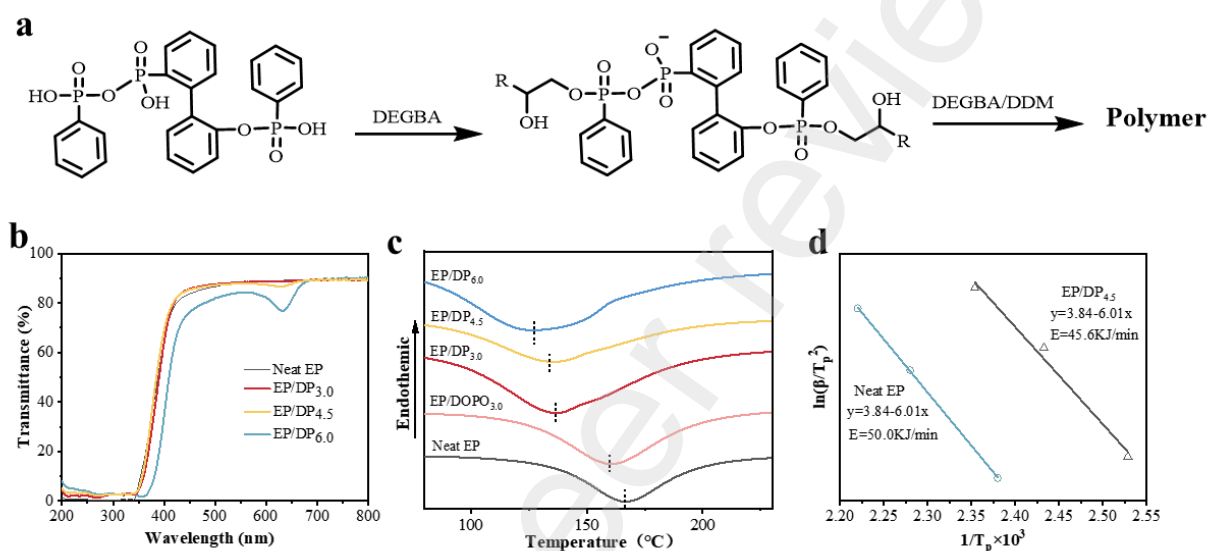
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137   **Figure 2**. (a) Curing promotion mechanism of DP. (b) Optical performance of

138   EP samples. (c) DSC curves of EP samples at a temperature increase rate of 10

139   K/min. (d) Kissinger method of fitting curves for EP and EP/DP$_{4.5}$.

140   **3.3. Curing Behavior analysis**

141   Through DSC test (Fig 3c, 3d), we found that the exothermic peak temperature

142   (T_p) of EP/DP was significantly reduced (from 166.7℃ to 128℃) compared with that

143   of Neat EP. Therefore, it is believed that the phosphate group affected by conjugation

144   and induction, due to its improved nucleophilicity, can participate in and significantly

145   promote the curing reaction (Fig 3a), shorten the curing time and reduce the energy

146   consumption, which is favorable for the industrial production of FREP[25]. The

147   Kissinger method provides empirical formulae commonly used to calculate the

148   apparent activation energy (E), and the positive effect of the phosphate groups in DP

9

149   on the curing reaction is argued by calculating a certain degree of reduction in the E

150   value for EP/DP$_{4.5}$[26].

151   **3.3. Thermal Properties**

152   We mainly examine the heat resistance and thermal stability of EP by dynamic

153   thermo-mechanical analysis (DMA) and thermogravimetric analysis (TGA), seen in

154   Fig 4a-d. and Table 2 respectively, the heat resistance of EP was mainly characterized

155   based on T_g. It is obvious that the introduction of DOPO causes a deterioration in the

156   heat resistance of EP due to the plasticizing effect[27].Compared to DOPO, the

157   addition of DP liquid does not adversely affect the heat resistance of EP. This is due

158   to the fact that DP unlock the large heterophenanthrene ring of DOPO, allowing it to

159   participate in the curing reaction to form a network structure and hindering the

160   relative movement between the molecular chains.

161   The cross-link density (V_e) of EP was calculated using the theoretical rubber

162   elasticity formula [25][28], and it was found that the introduction of DP could

163   significantly increase the V_e of EP, supporting our viewpoints above. In addition, the

164   rigidity of EP thermosets is generally characterized by the energy storage(E′) modulus

165   at 50 °C. The high polarity of DP can shorten the spacing of the EP molecule chains,

166   thus increasing the slip resistance and improving the stiffness of the system[29].
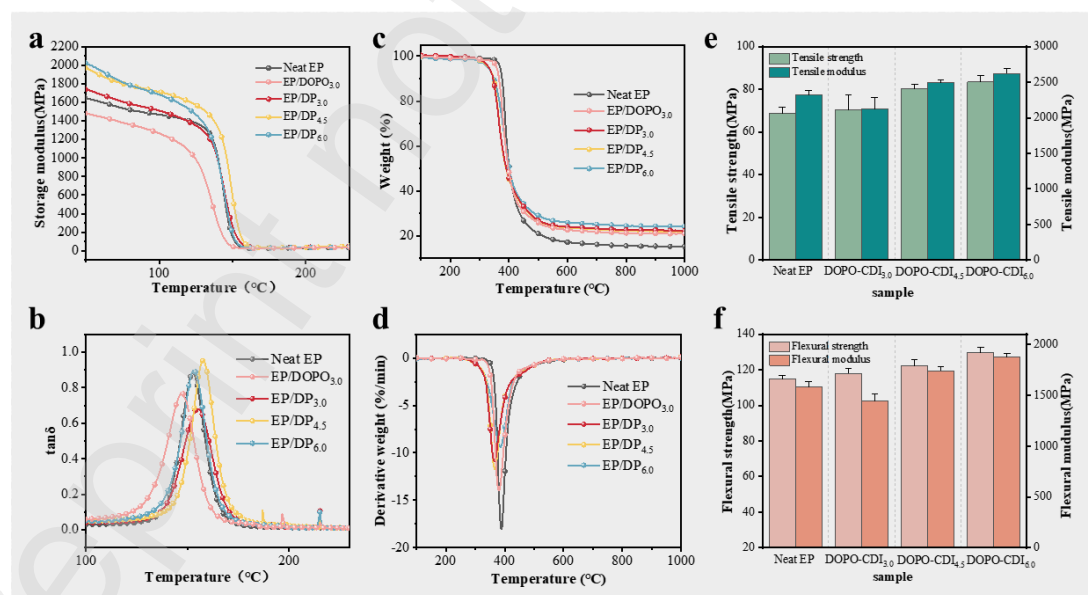
167   In the DTG test, it was observed from the test results that both DOPO and DP

168   advance the initial decomposition temperature ($T_{5\%}$) and the maximum mass loss

169   temperature (T_{Max}) of EP as a whole, it is a normal phenomenon of early

170   decomposition due to the introduction of weak bonds such as P-C and P-O

171   bonds[30][31]. We mainly used the maximum decomposition rate (R_{Max}) to

172   characterize the thermal stability of EP and found that the addition of DP liquid

173   resulted in a large reduction in R_{Max}. This is due to the fact that DP promotes charring

174   of EP and the phosphorus-containing graphitic layer formed on the air-exposed

175   surface can protect the substrate[6][32]. The large increase in thermal residual char

10

176 after the introduction of DP supports this viewpoint and it is worth noting that the

177 slightly lower residual carbon in EP/DP$_{4.5}$ compared to EP/DP$_{3.0}$ may be due to the

178 phosphorus effect (from 0.54 wt% to 0.81 wt%) insufficient to compensate for the

179 effect of the reduction in cross-linking density and modulus on the thermal

180 properties[25].

181 **Table 2. DMA and TGA Results of EP Thermosets**

Sample	T_g(°C)	E′ at 50°C(MPa)	V_e(mol/m^3)	R_{Max}(%/°C)	Char residue 1000°C(wt%)
Neat EP	153	1645	2572	18.1	15.2
EP/DOPO$_{3.0}$	147	1482	2579	14.0	20.4
EP/DP$_{3.0}$	155	1739	3203	10.9	22.3
EP/DP$_{4.5}$	158	1968	3157	11.7	21.8
EP/DP$_{6.0}$	157	1891	3087	9.4	24.2

182

183

184 **Figure 3**. (a) Curves of storage modulus and (b) loss modulus versus temperature. (c)

11

185   Curves of weight and (d) derivative weight as a function of temperature. (e) Tensile

186   and (f) Flexural Properties of EP Samples.

188   **3.4. Mechanical Properties**

189   Due to the good compatibility of DP with the matrix material, the introduction of

190   DP did not cause any deterioration in the mechanical properties, and the already

191   excellent mechanical properties of EP were further enhanced due to rigid matrix effect

192   and conjugation effect [33] [34]. The Fig 3e,3f. shows the results of our tests, where

193   the EP samples exhibit different levels of increase in each strength and modulus.

194   **3.5. Flame retardancy and combustion behavior of EP Thermosets**

195   Flame retardancy is one of the most valuable part of flame retarded epoxy (FREP),

196   however large amount of research based on FREPs is achieved by preparing flame

197   retardants with high flame retardancy efficiency or by adding a large amount of flame

198   retardant, which may result in a deterioration of the overall performance of the EP or

199   insufficient flame retardancy[1][35][36][37]. The high phosphorus content of DP liquid

200   (17.5wt%) addresses these potential issues and is an example of how flame retardants

201   can be added at low levels to achieve excellent flame retardancy and overall

202   performance.

203   As shown in Table 3, Neat EP has the worst flame retardancy and fails the vertical

204   flame test (UL-94), while after the introduction of DOPO, the flame retardancy

205   improves slightly but still fails to meet the UL-94 V-0 rating, with the deteriorating of

206   the overall properties. With the introduction of DP liquid, EP's limiting oxygen index

207   (LOI) increased dramatically, and can pass the UL-94 V-0 rating, only 6wt% can be

208   added to reach 41.2%LOI, the very high flame retardant efficiency of DP is attributed

209   to the high phosphorus content of DP liquid and the combined vapor phase[38] and

210   condensed phase[16] flame retardancy based on DOPO and PPOA. In addition, we

211   compare the flame retardant efficiencies of some of the excellent work cited in this

212   article with DP by means of scatter plots to intuitive arguments (Fig 4.).

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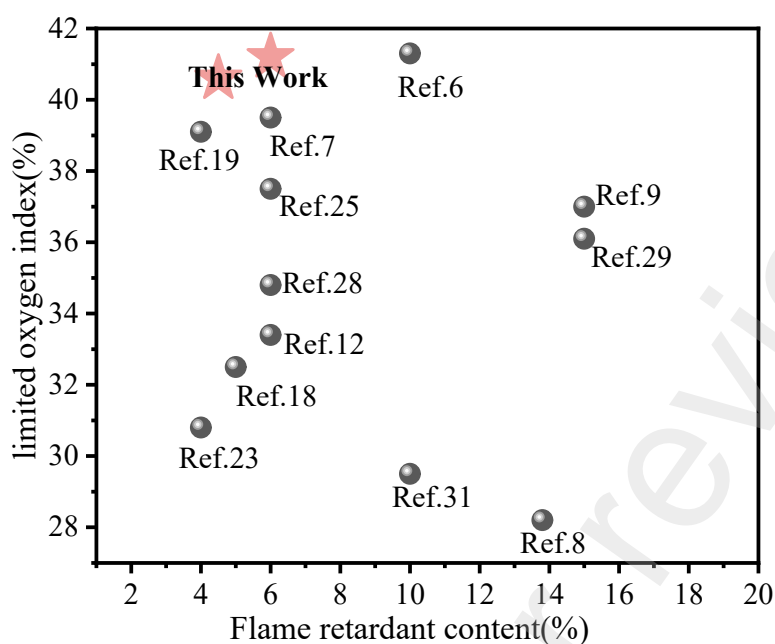
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214   **Figure 4**. Scatter Plot of Flame Retardant Efficiency Comparison of Flame

215   Retardants.

216   **Table 3. Flame retardancy of EP Thermosets**

Sample	P(wt%)	LOI(%)	UL-94	Dripping
Neat EP	0	26.4	NR	Yes
EP/DOPO$_{3.0}$	0.43	32.6	V-1	No
EP/DP$_{3.0}$	0.54	36.8	V-0	No
EP/DP$_{4.5}$	0.81	40.6	V-0	No
EP/DP$_{6.0}$	1.09	41.2	V-0	No

217   Cone calorimetry test is used to simulate the combustion behavior of the samples

218   under real fire conditions, and we have summarized the test results in Table 4 and Fig

219   5. First, the time to ignition (TTI) shows an overall decrease with the addition of

220   phosphorus-containing compounds, which is similar to the decrease in decomposition

14

221 temperatures in subsection 3.3, and is interpreted as the introduction of weak bonds to

222 promote early decomposition of the samples.

223   Peak heat release rate (PHRR) and total heat release rate (THR) are key

224 parameters used to measure the burning intensity of samples, the addition of DOPO

225 only slightly reduces the burning intensity[39], this is mainly due to the lack of

226 condensed phase flame retardant capability of DOPO[40], while DP strongly inhibits

227 the burning exotherm, the addition of only 6 wt% can reduce PHRR and THR by

228 52.4% and 45.2% respectively, which greatly improves the fire safety of EP.

229   The increase in the average carbon monoxide yield (Av-COY) and decrease in

230 the average carbon dioxide yield (Av-CO$_2$Y) with the introduction of DP indicates

231 incomplete combustion of FREP is intensified[41][42], which is attributed to the

232 excellent gas-phase flame retardancy of DP, allowing phosphorus-containing free

233 radicals generated by thermal decomposition effectively quench hydroxyl radicals

234 generated by combustion, thereby blocking the chain reaction of combustion.
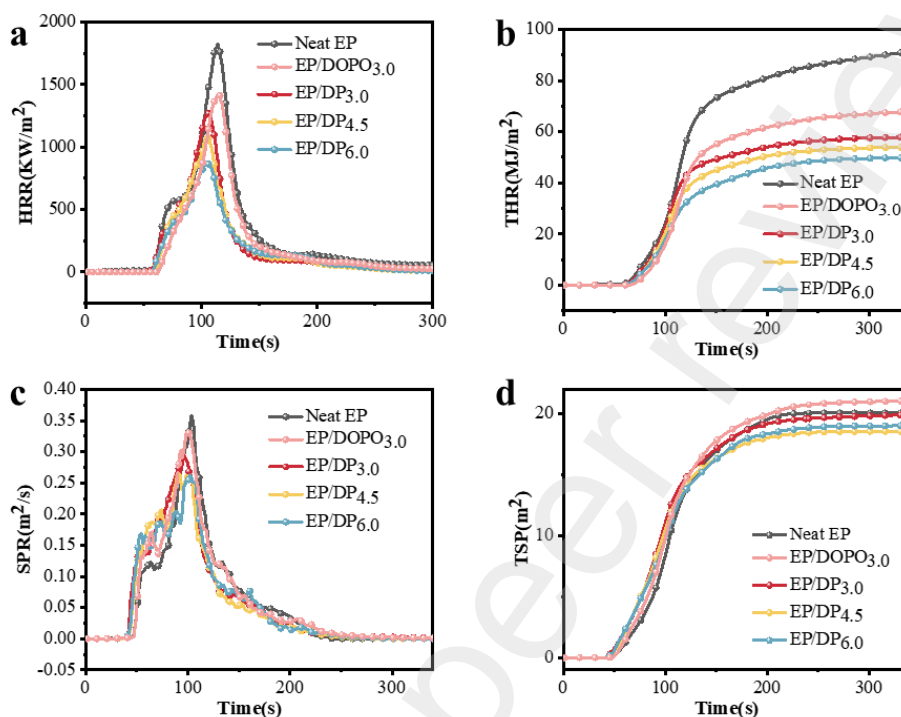
235   Surprisingly, the smoke inhibition effect of DP is not obvious, similar to that of

236 DOPO, and we suspect the main reason is that the flame retardant element of DP

237 liquid is single and the amount added is small. Therefore, the introduction of more

238 and suitable secondary flame retardants elements will be the main objective of the

239 next phase of our work.

240   **Table 4. combustion behavior of EP Thermosets**

Sample	Neat EP	EP/DOPO$_{3.0}$	EP/DP$_{3.0}$	EP/DP$_{4.5}$	EP/DP$_{6.0}$
TTI(s)	50	46	43	42	47
PHRR(KW/m^2)	1822.8	1416.2	1269.1	1079.2	867.6
THR(MJ/m^2)	91.3	69.4	58.2	54.3	50.0
Av-COY(kg/kg)	0.089	0.084	0.097	0.101	0.097
Av-CO$_2$Y(kg/kg)	2.16	1.44	1.37	1.31	1.56

15

PSPR(m²/s)	0.36	0.29	0.26	0.20	0.33
TSP(m²)	20.0	21.1	19.9	18.5	19.0

241

243 **Figure 5**. (a)HRR. (b)THR. (c)SPR. (d)TSP curves of EP thermosets obtained

244 from cone calorimetry.

245 **3.6. Condensed phase analysis**

246 In order to investigate the flame-retardant mechanism of DP based on the

247 condensed phase, we selected the most completely burnt part of sample after the cone

248 calorimetry test to perform a series of tests. First, we performed FTIR test on the

249 residual char(Fig 6a.), and it can be clearly observed that the residual char produced by

250 Neat EP has weak absorption peaks only in the region of the benzene ring. In contrast,

251 EP/DP$_{6.0}$ has prominent characteristic peaks of the benzene ring (1560 cm^{-1}, 1470 cm^{-1}

252 $^{-1}$) [41], while 1180 cm^{-1} and 880 cm^{-1} are attributed to P=O and P-O, respectively [42]

253 [43], in addition to the broad peak at 575 cm^{-1}, which is the absorption peak for the

254 formation of chemical bonds between elemental H and C or P. It is shown that the

16

255 introduction of DP can assist EP to construct a phosphorus-containing graphite layer

256 during the combustion process.

257   In order to further characterise the degree of graphitisation of our prepared FREP,

258 we performed Raman spectroscopy tests(Fig 6b, 6c.), and the double peaks in the

259 spectrum are the D-band (1339 cm-1) and the G-band (1584 cm-1), and their intensities

260 (ID, IG) were used to characterise the amount of amorphous and graphitised carbon,

261 respectively, and it can be observed that the ID/IG decreases significantly with the

262 introduction of DP[46], which further suggests that the cohesion of the DP phase flame

263 retardant effect is substantial.

264   We visualised the micromorphology of the EP samples by scanning electron

265 microscopy (Fig 6d.) and observed that the residual char produced by the combustion

266 of Neat EP was loose and full of holes, and therefore could not shield the exothermic

267 heat of combustion and protect the substrate as well. With the introduction of DP, the

268 residual carbon of EP became dense and flat, and the combustion exotherm was

269 suppressed. The above demonstrates the viewpoint about the excellent condensed phase

270 flame retardant effect of DP.

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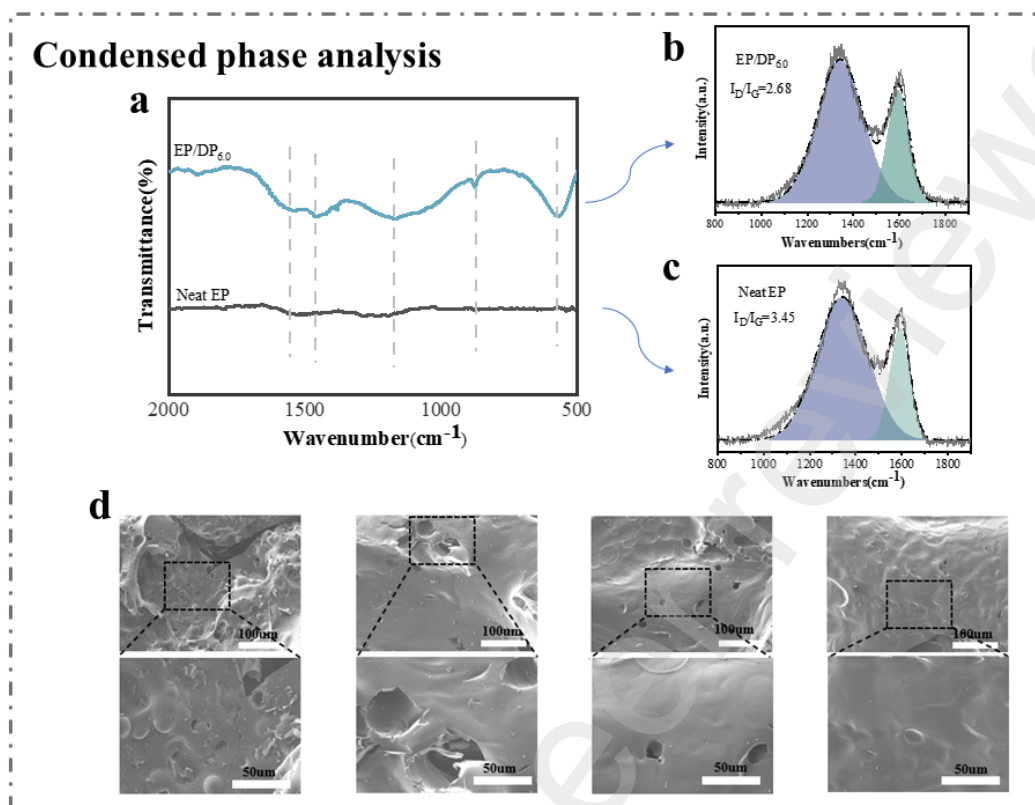
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274   **Figure 6**. (a) FTIR of EP/DP$_{6.0}$ and Neat EP combustion residues. (b) Raman

275   spectral fitting curve of EP/DP$_{6.0}$ and (c) Neat EP. (d) Microscopic morphology of

276   combustion residues of EP samples (100x and 270x).

277

18

278 **3.7 Vapor phase analysis**

279   The vapor phase flame retardant effect of DP was investigated by Py-GC/MS and

280 TG-IR. It can be observed by Fig 7a-c that the vapor phase products of DP thermally

281 cracked under nitrogen atmosphere are relatively homogeneous, mainly consisting of

282 DOPO fragments, radicals, water and gases, which is attributed to the ability of PPOA

283 fragments to promote dehydration and catalytic charring [47][48], and the formation of

284 DOPO by thermal dehydration of HPPA is the main reason for the flame retardant effect

285 of DP in the vapor phase.

286   We further investigated the vapor phase flame retardant mechanism of DP by TG-

287 IR and observed from Fig 7d. that in addition to water and alkanes, a large amount of

288 phosphorus-containing substances are released from $EP/DP_{6.0}$ at high temperatures,

289 such as fragments containing P-C ($1515cm^{-1}$) and P=O ($1260cm^{-1}$) captured by

290 FTIR[6][49], which are eventually converted into phosphorus-containing radicals at

291 elevated temperatures and play the role of quenching combustion radicals and

292 interrupting the chain reaction of combustion, thus reducing the intensity of combustion,

293 which reduce the intensity of combustion. Finally, we summarize the design concept

294 and mechanism of action of DP in Fig 8.
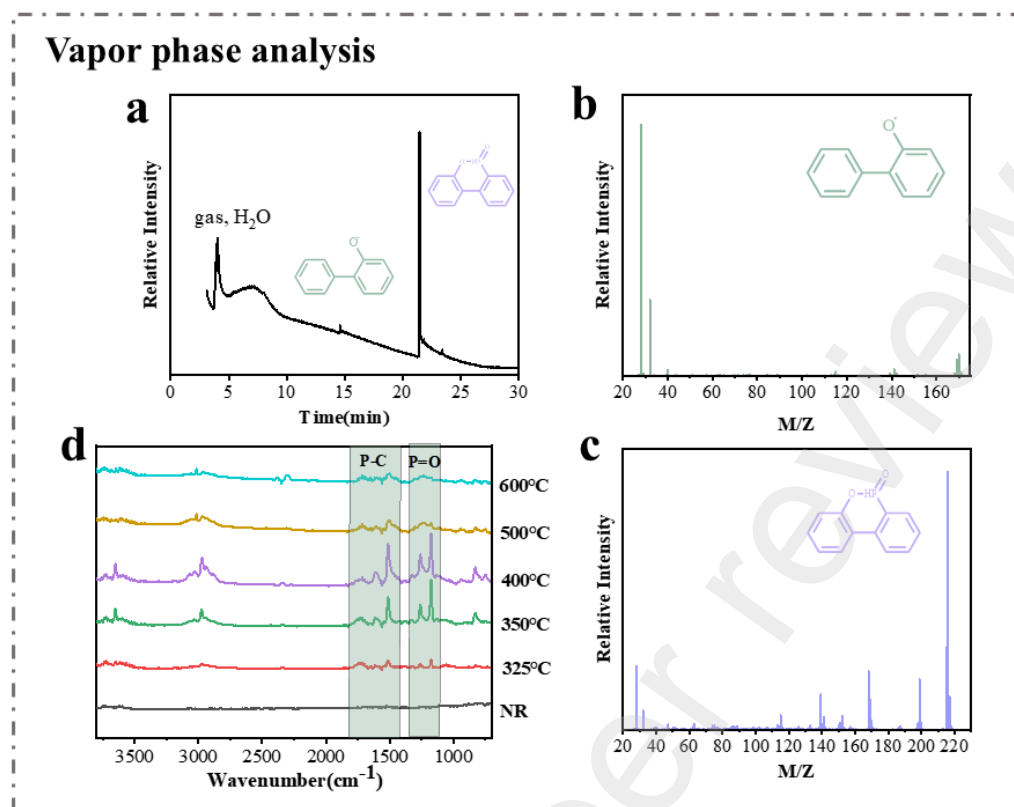
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Figure 7. (a)Thermal cleavage Py-GC/MS spectra of DP. (b)Partial radical fragments and (c)DOPO fragments from thermal cleavage. (d)TG-IR spectrum of EP/DP$_{6.0}$.

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Due to the excellent catalytic charring ability of PPOA, DP is able to re-form DOPO when heated, thus avoiding the adverse effect of DOPO on the material performances while providing the gas-phase flame retardant effect of DOPO.

Figure 8. DP design concept and mechanism of action.

4. CONCLUSIONS

301
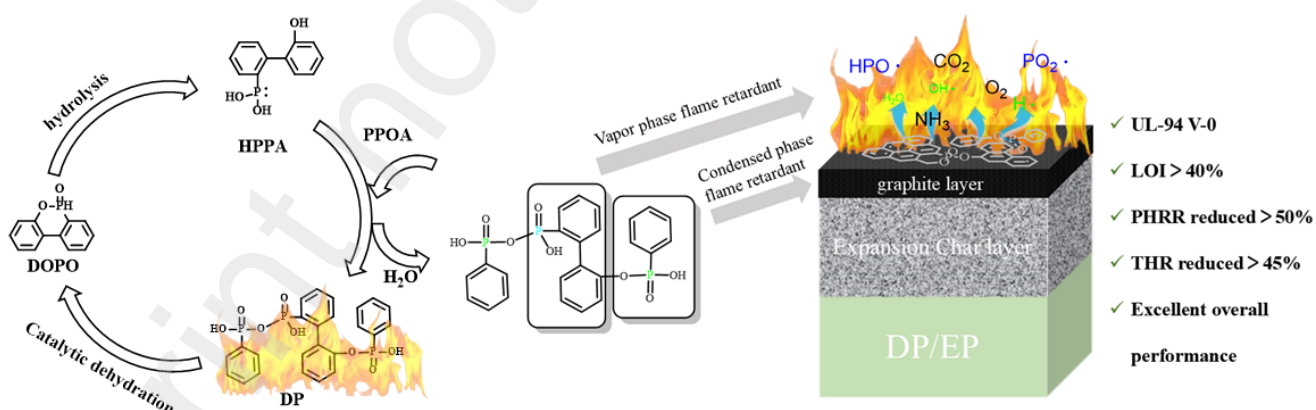
302   This work proposes a novel flame retardant precursor, HPPA, obtained by
303 hydrolysis of DOPO. Our HPPA-based liquid flame retardant DP is structurally similar
304 to EP, which is easier to dissolve in EP monomers and form chemical bonds with EP,
305 thus obtaining excellent processing, thermal and mechanical properties.

306   The most attractive feature of DP is its excellent flame retardancy, it has both gas
307 phase and condensed phase flame retardancy based on HPPA fragments and PPOA
308 fragments, and has a phosphorus content up to 17.5wt%, which makes it achievable to
309 obtain excellent flame retardancy by adding only 6wt% of DP to EP, with its LOI
310 reaching over 40% and its PHRR and THR being reduced by 52.4% and 45.2%
311 respectively. We believe that DP is expected to replace DOPO and become widely used
312 in the epoxy resin industry.

313 **Data Availability Statement**

314   The data presented in this study are available on request from the corresponding
315 author.

316 **Conflicts of Interest:**

317   The authors declare no conflict of interest.

319 Reference

[1] Huo S, Song P, Yu B, et al. Phosphorus-containing flame retardant epoxy thermosets: Recent

321 advances and future perspectives[J]. Progress in Polymer Science, 2021, 114: 101366.

[2] Huo S, Liu Z, Wang J. Thermal properties and flame retardancy of an intumescent flame-

323 retarded epoxy system containing phosphaphenanthrene, triazine-trione and piperidine[J].

324 Journal of Thermal Analysis and Calorimetry, 2020, 139: 1099-1110.

[3] Li X, Liang J, Shi T, et al. Tribological behaviors of vacuum hot-pressed ceramic composites

326 with enhanced cyclic oxidation and corrosion resistance[J]. Ceramics International, 2020,

327 46(9): 12911-12920.

[4] Shi X H, Li X L, Li Y M, et al. Flame-retardant strategy and mechanism of fiber reinforced

329 polymeric composite: a review[J]. Composites Part B: Engineering, 2022, 233: 109663..

[5] Wang J, Wang J, Yang S, et al. Single-component flame-retardant and smoke-suppressive

331 epoxy resins enabled by an aluminum/phosphorus/imidazole-containing complex[J].

332 Composites Part B: Engineering, 2023, 253: 110571.

[6] Peng X, Li Z, Wang D, et al. A facile crosslinking strategy endows the traditional additive

334 flame retardant with enormous flame retardancy improvement[J]. Chemical Engineering

335 Journal, 2021, 424: 130404.

[7] Liu X F, Xiao Y F, Luo X, et al. Flame-Retardant multifunctional epoxy resin with high

337 performances[J]. Chemical Engineering Journal, 2022, 427: 132031.

[8] Wang J, Wang J, Yang S, et al. Multifunctional phosphorus-containing imidazoliums

339 endowing one-component epoxy resins with superior thermal latency, heat resistance,

340 mechanical properties, and fire safety[J]. Chemical Engineering Journal, 2024, 485: 149852.

[9] Xu Y J, Shi X H, Lu J H, et al. Novel phosphorus-containing imidazolium as hardener for

342 epoxy resin aiming at controllable latent curing behavior and flame retardancy[J]. Composites

343 Part B: Engineering, 2020, 184: 107673.

[10] Zhang Y C, Xu G L, Liang Y, et al. Preparation of flame retarded epoxy resins containing

345 DOPO group[J]. Thermochimica Acta, 2016, 643: 33-40.

[11] Yang Y, Wang D Y, Jian R K, et al. Chemical structure construction of DOPO-containing

22

347   compounds for flame retardancy of epoxy resin: A review[J]. Progress in Organic Coatings,

348   2023, 175: 107316.

349 [12] He X, Zhang W, Yang R. The characterization of DOPO/MMT nanocompound and its effect

350   on flame retardancy of epoxy resin[J]. Composites Part A: Applied Science and Manufacturing,

351   2017, 98: 124-135.

352 [13] Wang C S, Shieh J Y. Synthesis and properties of epoxy resins containing 2-(6-oxid-6H-

353   dibenz< c, e>< 1, 2> oxaphosphorin-6-yl) 1, 4-benzenediol[J]. Polymer, 1998, 39(23): 5819-

354   5826.

355 [14] Laoutid F, Bonnaud L, Alexandre M, et al. New prospects in flame retardant polymer materials:

356   From fundamentals to nanocomposites[J]. Materials science and engineering: R: Reports, 2009,

357   63(3): 100-125.

358 [15] Hamdani S, Longuet C, Perrin D, et al. Flame retardancy of silicone-based materials[J].

359   Polymer Degradation and Stability, 2009, 94(4): 465-495.

360 [16] Bifulco A, Varganici C D, Rosu L, et al. Recent advances in flame retardant epoxy systems

361   containing non-reactive DOPO based phosphorus additives[J]. Polymer Degradation and

362   Stability, 2022, 200: 109962.

363 [17] Jiang Q, Li P, Liu Y, et al. Flame retardant cotton fabrics with anti-UV properties based on tea

364   polyphenol-melamine-phenylphosphonic acid[J]. Journal of colloid and interface science,

365   2023, 629: 392-403.

366 [18] Rong H, Guo Y, Chen Z, et al. Synergistic effect of phenyl phosphoric acid derivatives and

367   DOPO on multifunctional epoxy resin: Fire safety, mechanical properties, transparency and

368   hydrophobicity[J]. Polymer Degradation and Stability, 2023, 216: 110471.

369 [19] Jin S, Qian L, Qiu Y, et al. High-efficiency flame retardant behavior of bi-DOPO compound

370   with hydroxyl group on epoxy resin[J]. Polymer degradation and stability, 2019, 166: 344-352.

371 [20] Kandola B K, Magnoni F, Ebdon J R. Flame retardants for epoxy resins: Application‑related

372   challenges and solutions[J]. Journal of Vinyl and Additive Technology, 2022, 28(1): 17-49.

373 [21] Zhang L Y, Song W M, Liu Y. Simple modification of phenylphosphonic acid to construct

23

374   polyester-cotton fabrics with high flame retardancy[J]. Advanced Industrial and Engineering

375   Polymer Research, 2024.

376 [22] Meng D, Ma Z, Leng Q, et al. A flame-retardant DOPO-MgAl-LDH was prepared and applied

377   in poly (methyl methacrylate) resin[J]. Polymers for Advanced Technologies, 2020, 31(1): 73-

378   85.

379 [23] Yu L, Huo S, Wang C, et al. Flame-retardant poly (L-lactic acid) with enhanced UV protection

380   and well-preserved mechanical properties by a furan-containing polyphosphoramide[J].

381   International Journal of Biological Macromolecules, 2023, 234: 123707.

382 [24] Tibiletti L, Longuet C, Ferry L, et al. Thermal degradation and fire behaviour of unsaturated

383   polyesters filled with metallic oxides[J]. Polymer Degradation and Stability, 2011, 96(1): 67-

384   75.

385 [25] Liu P, Wang X, Huang J, et al. Halogen-free epoxy flame retardant & promoter with

386   diimidazole skeleton improves overall properties of epoxy resins[J]. Chemical Engineering

387   Journal, 2024: 155408.

388 [26] Blaine R L, Kissinger H E. Homer Kissinger and the Kissinger equation[J]. Thermochimica

389   acta, 2012, 540: 1-6.

390 [27] Butnaru I, Fernández-Ronco M P, Czech-Polak J, et al. Effect of meltable triazine-DOPO

391   additive on rheological, mechanical, and flammability properties of PA6[J]. Polymers, 2015,

392   7(8): 1541-1563.

393 [28] Huo S, Sai T, Ran S, et al. A hyperbranched P/N/B-containing oligomer as multifunctional

394   flame retardant for epoxy resins[J]. Composites Part B: Engineering, 2022, 234: 109701.

395 [29] Lou S, Wang S, Zhang L, et al. Intrinsic flame-retardant epoxy resin based on phosphorus-

396   containing liquid imidazole compound: Simultaneously improving fire safety, mechanical

397   property and heat resistance[J]. Chemical Engineering Journal, 2024: 152816.

398 [30] Yang H, Shi B, Xue Y, et al. Molecularly engineered lignin-derived additives enable fire-

399   retardant, UV-shielding, and mechanically strong polylactide biocomposites[J].

400   Biomacromolecules, 2021, 22(4): 1432-1444.

401   [31] Zhang A, Zhang J, Liu L, et al. Engineering phosphorus-containing lignin for epoxy

402   biocomposites with enhanced thermal stability, fire retardancy and mechanical properties[J].

403   Journal of Materials Science & Technology, 2023, 167: 82-93.

404   [32] Liu L, Shi B, Zhang A, et al. A polyphosphoramide-grafted lignin enabled thermostable and

405   fire-retardant polylactide with preserved mechanical properties[J]. Composites Part A: Applied

406   Science and Manufacturing, 2022, 160: 107028.

407   [33] Wang W, Yu B, Zhang Y, et al. Fully aminated rigid-rod aramid reinforced high strength epoxy

408   resin and its composite with carbon fibers[J]. Composites Science and Technology, 2022, 221:

409   109324.

410   [34] Wang P, Xiao H, Duan C, et al. Sulfathiazole derivative with phosphaphenanthrene group:

411   synthesis, characterization and its high flame-retardant activity on epoxy resin[J]. Polymer

412   degradation and stability, 2020, 173: 109078.

413   [35] Lou S, Wang S, Zhang L, et al. Intrinsic flame-retardant epoxy resin based on phosphorus-

414   containing liquid imidazole compound: Simultaneously improving fire safety, mechanical

415   property and heat resistance[J]. Chemical Engineering Journal, 2024: 152816.

416   [36] Zhi M, Yang X, Fan R, et al. A comprehensive review of reactive flame-retardant epoxy resin:

417   fundamentals, recent developments, and perspectives[J]. Polymer Degradation and Stability,

418   2022, 201: 109976.

419   [37] Liu Q, Wang D, Li Z, et al. Recent developments in the flame-retardant system of epoxy

420   resin[J]. Materials, 2020, 13(9): 2145.

421   [38] Varganici C D, Rosu L, Bifulco A, et al. Recent advances in flame retardant epoxy systems

422   from reactive DOPO−based phosphorus additives[J]. Polymer Degradation and Stability, 2022,

423   202: 110020.

424   [39] Huo S, Song P, Yu B, et al. Phosphorus-containing flame retardant epoxy thermosets: Recent

425   advances and future perspectives[J]. Progress in Polymer Science, 2021, 114: 101366.

426   [40] Levchik S V, Weil E D. Thermal decomposition, combustion and flame‑retardancy of epoxy

427   resins—a review of the recent literature[J]. Polymer International, 2004, 53(12): 1901-1929.

428   [41] Wang P, Chen L, Xiao H, et al. Nitrogen/sulfur-containing DOPO based oligomer for highly

429   efficient flame-retardant epoxy resin[J]. Polymer Degradation and Stability, 2020, 171: 109023.

430   [42] Huo S, Wang J, Yang S, et al. Synthesis of a novel phosphorus-nitrogen type flame retardant

431   composed of maleimide, triazine-trione, and phosphaphenanthrene and its flame retardant

432   effect on epoxy resin[J]. Polymer Degradation and Stability, 2016, 131: 106-113.

433   [43] Rao W, Zhao P, Yu C, et al. High strength, low flammability, and smoke suppression for epoxy

434   thermoset enabled by a low-loading phosphorus-nitrogen-silicon compound[J]. Composites

435   Part B: Engineering, 2021, 211: 108640.

436   [44] Luo H, Rao W, Zhao P, et al. An efficient organic/inorganic phosphorus−nitrogen−silicon

437   flame retardant towards low-flammability epoxy resin[J]. Polymer Degradation and Stability,

438   2020, 178: 109195.

439   [45] Zhong L, Li T, Zhang J, et al. Simultaneously improving the flame retardancy and toughness

440   of epoxy composites with hyperbranched phosphorus-containing polysiloxane functionalized

441   halloysite nanotubes[J]. European Polymer Journal, 2022, 179: 111564.

442   [46] Huo S, Zhou Z, Jiang J, et al. Flame-retardant, transparent, mechanically-strong and tough

443   epoxy resin enabled by high-efficiency multifunctional boron-based polyphosphonamide[J].

444   Chemical Engineering Journal, 2022, 427: 131578.

445   [47] Ran S, Ye R, Cai Y, et al. Synergistic flame retardant mechanism of lanthanum

446   phenylphosphonate and decabromodiphenyl oxide in polycarbonate[J]. Polymer Composites,

447   2019, 40(3): 986-999.

448   [48] Jiang Q, Li P, Liu Y, et al. Flame retardant cotton fabrics with anti-UV properties based on tea

449   polyphenol-melamine-phenylphosphonic acid[J]. Journal of colloid and interface science,

450   2023, 629: 392-403.

451   [49] Zou J, Duan H, Chen Y, et al. AP/N/S-containing high-efficiency flame retardant endowing

452   epoxy resin with excellent flame retardance, mechanical properties and heat resistance[J].

453   Composites Part B: Engineering, 2020, 199: 108228.

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Table 1. The formulations of epoxy thermosets

Sample	DGEBA(wt %)	DDM(wt%)	DP(wt%)	P(wt%)
Neat EP	80	20	0	0
EP/DOPO3.0	77.6	19.4	3.0	0.43
EP/DP3.0	77.6	19.4	3.0	0.53
EP/DP4.5	76.4	19.1	4.5	0.79
EP/DP6.0	75.2	18.8	6.0	1.05

Table 2. DMA and TGA Results of EP Thermosets

Sample	T_g(℃)	E′ at 50℃(MPa)	V_e(mol/m^3)	R_{Max}(%/℃)	Char residue 1000℃(wt%)
Neat EP	153	1645	2572	18.1	15.2
EP/DOPO$_{3.0}$	147	1482	2579	14.0	20.4
EP/DP$_{3.0}$	155	1739	3203	10.9	22.3
EP/DP$_{4.5}$	158	1968	3157	11.7	21.8
EP/DP$_{6.0}$	157	1891	3087	9.4	24.2

Table 3. Flame retardancy of EP Thermosets

Sample	P(wt%)	LOI(%)	UL-94	Dripping
Neat EP	0	26.4	NR	Yes
EP/DOPO$_{3.0}$	0.43	32.6	V-1	No
EP/DP$_{3.0}$	0.54	36.8	V-0	No
EP/DP$_{4.5}$	0.81	40.6	V-0	No
EP/DP$_{6.0}$	1.09	41.2	V-0	No

Table 4. combustion behavior of EP Thermosets

Sample	Neat EP	EP/DOPO$_{3.0}$	EP/DP$_{3.0}$	EP/DP$_{4.5}$	EP/DP$_{6.0}$
TTI(s)	50	46	43	42	47
PHRR(KW/m^2)	1822.8	1416.2	1269.1	1079.2	867.6
THR(MJ/m^2)	91.3	69.4	58.2	54.3	50.0
Av-COY(kg/kg)	0.089	0.084	0.097	0.101	0.097
Av-CO$_2$Y(kg/kg)	2.16	1.44	1.37	1.31	1.56
PSPR(m^2/s)	0.36	0.29	0.26	0.20	0.33
TSP(m^2)	20.0	21.1	19.9	18.5	19.0