

Research Article

Phosphorus Flame Retardants for Polymeric Materials from Gallic Acid and Other Naturally Occurring Multihydroxybenzoic Acids

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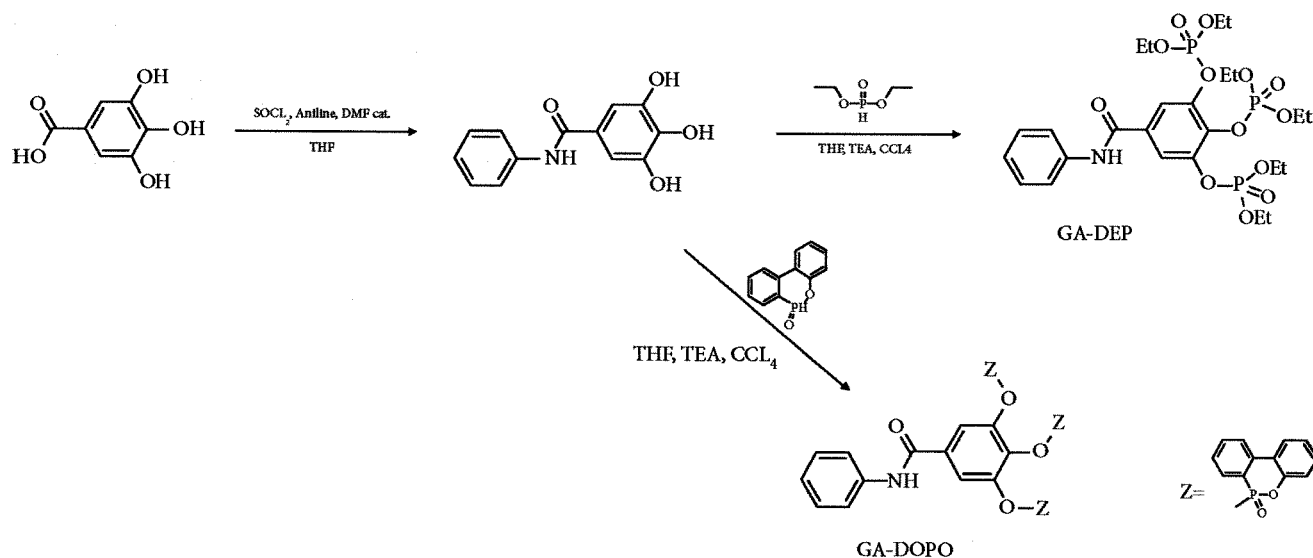
The development of polymer and polymer additives from renewable biosources is becoming increasingly prominent. This reflects increasing concerns about sustainability, environmental quality, and human health. Bioproducts produced in nature are generally inexpensive and benign in the environment. Moreover, degradation of derivatives does not yield toxic products. Gallic acid (3,4,5-trihydroxybenzoic acid) is found widely in nature and has long been touted for its medicinal qualities. 3,5-Dihydroxybenzoic acid is also produced by several plants, most notably buckwheat. Both compounds, as the anilide and methyl ester, respectively, have been converted to a series of phosphorus esters, both phosphonate and phosphate. Esters have been fully characterized using spectroscopic and thermal methods. These compounds display good flame retardancy at low loadings in DGEBA epoxy resin.

1. Introduction

There is an increasing reliance on natural biosources as precursors to polymers and polymer additives [1–11]. This is particularly the case for plasticizers [12–14] and flame retardants [15–17]. These developments are driven by an increasing concern for sustainability, environmental quality, and human health. The release of potentially toxic agents into the environment is increasingly unacceptable. Traditionally, organohalogen compounds, particularly brominated aromatics, have been widely used as effective flame retardants [18]. However, these compounds often migrate from the polymer matrix into which they have been incorporated. Brominated aromatics are stable in the natural environment, tend to bioaccumulate, are increasingly finding their way into the human diet, and may pose health risks [18–22]. To reduce the propensity for migration from the polymer matrix, oligomeric flame retardants containing brominated units have been developed [23, 24]. These materials can function as effective flame retardants both in the presence and in the absence of an antimony oxide promoter. However, they suffer from the perception that halogens are undesirable

established by the behavior of lower molecular weight counterparts. These smaller compounds continue to face increasing regulatory pressure and legislative restriction [25–27]. Replacements for these compounds are actively being sought. Phosphorus compounds offer great potential as acceptable flame retardants [28]. In general, phosphorous compounds are less toxic than the materials that they are replacing [29, 30]. Phosphorus flame retardants derived from renewable biomolecules are particularly attractive [17]. Starting materials obtained from natural sources are usually non-toxic and environmentally benign. Costs are independent of fluctuations in petrochemical markets.

Gallic acid (3,4,5-trihydroxybenzoic acid) is widely produced in nature and may be extracted from gallnuts, oak bark, several legumes, grapes, berries, hickory nuts, and walnuts [31, 32]. Gallic acid has long been touted for its medicinal properties. When consumed, it acts as an antioxidant to help prevent potential cardiac dysfunction and the formation of radical oxygen species which disrupt cell membranes [33]. Many pharmaceuticals utilize the anti-inflammatory, anticarcinogenic, and radio-protective nature of gallic acid for the treatment of a variety of diseases [34–36].



SCHEME 1: Synthesis of phosphorus esters of gallic acid.

TABLE 1: Thermal decomposition of phosphorous esters of gallic acid anilide.

Compound	Temperature of decomposition onset (°C) ^a		Temperature of maximum decomposition rate (°C)		Decomposition residue (%) ^b	
	Nitrogen	Air	Nitrogen	Air	Nitrogen	Air
GA-DEP	239	175	253	205	37	13
GA-DOPO	316	313	373	366	18	7

^aExtrapolated onset temperature from the derivative plot of mass loss versus temperature. ^bPercentage of the initial sample mass.

As a precursor to flame retardants, it offers three hydroxyl groups which may be subjected to esterification. Because the three hydroxyls occupy adjacent positions on the aromatic nucleus, it is not always possible to generate the corresponding triester, depending on the steric requirements of the groups being introduced. This may be overcome by first converting a gallic ester derivative to triacrylate followed by the Michael addition of phosphite [37]. Alternatively, a polyhydroxy aromatic acid with nonadjacent hydroxyl groups can be used. 3,5-Dihydroxybenzoic acid is a naturally occurring acid found in numerous plants and grains, most notably buckwheat [38–41]. Both gallic acid and 3,5-dihydroxybenzoic acid have been converted to derivatives, anilide and methyl ester, respectively, suitable for use as phosphorus ester precursors. The phosphorus esters generated display good flame-retarding properties in polymeric matrices.

2. Experiment

2.1. Materials. Common solvents and reagents were obtained from Thermo Fisher Scientific or the Aldrich Chemical Company. Tetrahydrofuran (THF) was distilled from lithium aluminum hydride prior to use, and methylene chloride from calcium hydride. Gallic acid, 3,5-dihydroxybenzoic acid, carbon tetrachloride, triethylamine, diethylphosphite, and aniline were obtained from the Aldrich Chemical Company. 9,10-Dihydro-9-oxa-10-phosphaphenanthrene-

10-oxide (DOPO) was from TCI. Diphenyl chlorophosphate was provided by ICL-IP America Inc. The diglycidyl ether of *bis*-phenol A (DGEBA) was supplied by the Dow Chemical Company.

2.2. Methods and Instrumentation. General methods and instrumentation have been previously described [17, 42, 43]. Nuclear magnetic resonance (NMR) spectra were obtained using a Varian Mercury 300 MHz or INOVA 500 MHz spectrometer. Tetramethylsilane was used as an internal reference ($\delta = 0.00$) for proton and carbon spectra, and triphenylphosphate ($\delta = -18.00$) for phosphorus spectra. Infrared spectra were recorded using a Thermo Scientific Nicolet 380 FTIR spectrometer. Thermal transitions were determined by differential scanning calorimetry (DSC) using a TA Instruments Q2000 instrument. Thermal stability was assessed by thermogravimetry using a TA Instruments Q500 instrument. Peak heat release rates were determined using a microscale combustion calorimeter (ASTM D7309a) (Fire Testing Technology Ltd. (FTT)). Values reported are the averages of five determinations with a deviation of less than 5%. Limiting oxygen index values were determined using an FTT Oxygen Index unit (ASTM D2863-13). Vertical burn tests were conducted in an FTT test chamber (ASTM D2863-06).

2.3. Test Specimen. Samples for flammability testing were prepared as previously described [42].

2.4. Synthesis

2.4.1. 3,4,5-Trihydroxybenzanilide. Gallic acid chloride was synthesized by the dropwise addition, over a period of 0.25 hr, of 3.16 ml (44.3 mmol) of thionyl chloride to a solution of 5.03 g (29.6 mmol) of gallic acid and three drops of dimethylformamide in 20 ml of anhydrous tetrahydrofuran (THF) maintained near 0°C (external ice bath). Upon completion of the addition, the mixture was stirred near 0°C for an additional 0.25 hr. The progress of the reaction was monitored by periodic removal of aliquots for analysis using infrared spectroscopy. Upon observation of the complete conversion of acid to acid chloride, 10.8 ml (118.0 mmol) of aniline was added dropwise over a period of 0.25 hr to the stirred solution. Upon completion of the addition, the solution was allowed to slowly warm to room temperature. The progress of the reaction was monitored by periodic removal of an aliquot of the mixture for analysis using infrared spectroscopy. The reaction was completed within 12 hr. Anilinium chloride was removed by filtration at reduced pressure. The filtrate was diluted with 200 ml of ethyl acetate and washed, successively, with 50 ml of water, 50 ml of 10% aqueous hydrochloric acid solution, 50 ml of 10% aqueous sodium hydroxide solution, and 50 ml of saturated aqueous sodium chloride solution. The ethyl acetate solution was dried over anhydrous sodium sulfate, and the solvent was removed by rotary evaporation at reduced pressure. The residual solid was recrystallized from water to afford 6.37 g (88.1% yield) of 3,4,5-trihydroxybenzanilide as a pale yellow solid: mp 210°C (DSC); ESI-MS, 246 g/mol; IR (cm^{-1}) 3490 (s) N-H, 3533 (s, broad) O-H, 1636 (s) amide C=O, 1593 (s) aromatic nucleus; $^1\text{H-NMR}$ (δ DMSO- d_6) 7.26 (m, 7H), 8.78 (s, 1H), 9.14 (s, 2H), 9.87 (s, 1H); ^{13}C NMR (δ , DMSO- d_6) 127.2 (m, aromatic carbon atoms), 166.0 (s, carbonyl carbon atom).

2.4.2. Methyl 3,5-Dihydroxybenzoate. A solution of 10.0 g (64.9 mmol) of 3,5-dihydroxybenzoic acid in 200 ml of methanol containing (0.35 ml, 0.64 g, 6.49 mmol) concentrated aqueous sulfuric acid solution was stirred at solvent reflux. The progress of the reaction was monitored by periodic removal of an aliquot of the reaction mixture for analysis using infrared spectroscopy (changes in the carbonyl region of the spectrum). The reaction was completed within 10 hr. Excess methanol was removed by rotary evaporation at reduced pressure to provide oil which was dissolved in 450 ml of ethyl acetate. The resulting solution was washed, successively, with two 40 ml portions of saturated aqueous sodium bicarbonate solution and 40 ml of saturated aqueous sodium chloride solution. The solution was dried over anhydrous sodium sulfate, and the solvent was removed by rotary evaporation at reduced pressure to afford a fine white solid. This material was dried overnight at 15 torr and 50°C to provide 9.08 g (90.8% yield) of methyl 3,5-dihydroxybenzoate: IR (cm^{-1}) 3229 (s, br) phenolic hydroxyl, 3089 (m) $\text{C}_{\text{sp}2}\text{-H}$, 2952 (m) $\text{C}_{\text{sp}3}\text{-H}$, 1687 (s) ester C=O, 1600 (s) aromatic nucleus; ^1H NMR (δ , DMSO- d_6) 3.76 (s, 3H, methoxyl protons), 6.41 (t, 1H) and 6.79 (d, 2H) aromatic protons, 9.10 (br, s, 2H, hydroxyl protons); ^{13}C (δ , DMSO- d_6) 52.4

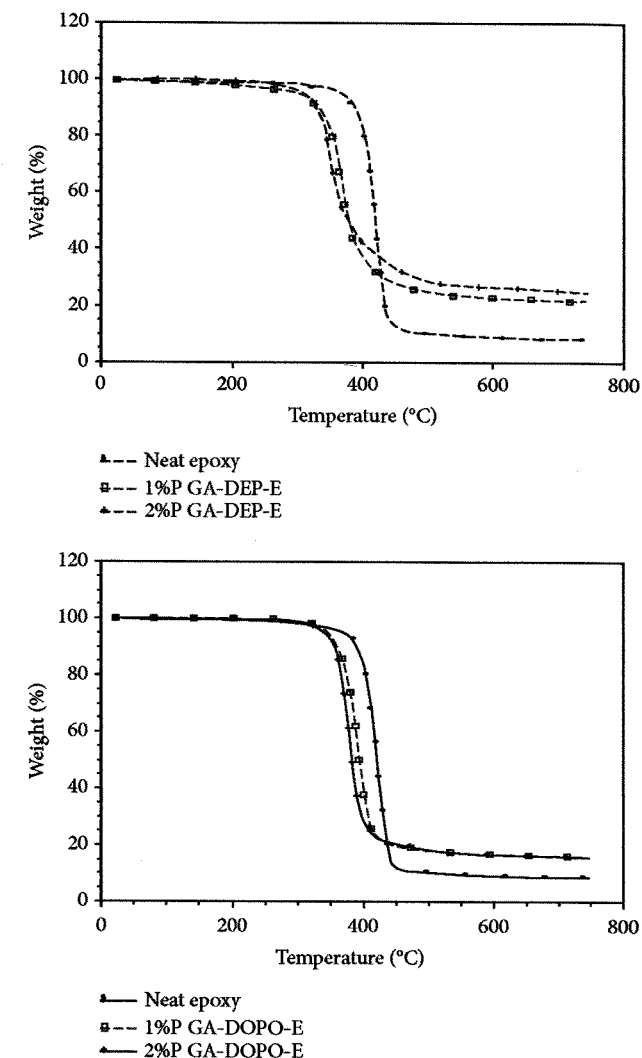


FIGURE 1: Thermal stability of blends of phosphorus esters of gallic acid anilide with DGEBA epoxy.

(methoxy carbon atom), 107.5, 131.7, 158.9 (aromatic carbon atoms), 166.7 (ester carbonyl carbon atom).

Both the anilide and benzoate ester were converted to the corresponding phosphorus esters using methods previously described [42]. In general, the appropriate phenolic compound was treated with a phosphite in the presence of carbon tetrachloride (Atherton-Todd procedure). For the preparation of the diphenyl phosphate ester, diphenyl chlorophosphate was used as a reagent.

2.4.3. 3,4,5-Tri(diethylphosphato)benzanilide. Into a 500 ml three-necked, round-bottomed flask fitted with a magnetic stirring bar, a dropping funnel, and a Liebig condenser bearing a gas-inlet tube were placed 5.53 g (49.0 mmol) of diethylphosphite, 2.71 g (11.0 mmol) of 3,4,5-trihydroxybenzanilide, 5.98 ml (42.9 mmol) of triethylamine, and 300 ml of ethyl acetate. The solution was stirred near 0°C (external ice bath) as 5.37 ml (55.9 mmol) of carbon tetrachloride was added, dropwise, over a period of five minutes. The progress of the reaction was monitored by periodic removal of an

TABLE 2: Thermal degradation of blends of phosphorous esters of gallic acid anilide with DGEBA epoxy.

Blend	Level of additive in blend (%)	Level of phosphorous in blend (%)	Decomposition onset temperature (°C) ^a		Temperature of maximum decomposition rate (°C)		Decomposition residue (%) ^b	
			Nitrogen	Air	Nitrogen	Air	Nitrogen	Air
DGEBA epoxy	0	0	390	374	423	408	8	8
GA-DEP-E	7.5	1	342	349	370	371	22	4
GA-DEP-E	15.0	2	327	334	352	354	25	6
GA-DOPO-E	9.6	1	360	372	394	392	16	3
GA-DOPO-E	19.1	2	348	353	381	375	16	3

^aExtrapolated onset temperature from the derivative plot of mass/loss versus temperature. ^bPercentage of the initial sample mass.

TABLE 3: Glass transition temperatures for blends of phosphorus esters of gallic acid anilide with DGEBA epoxy resin.

Blend	Phosphorous level (%)	Additive by weight (%)	T_g (°C)
DGEBA epoxy	0	0	110
GA-DEP-E	1	7.5	129
	2	14.0	148
GA-DOPO-E	1	9.6	145
	2	19.1	142

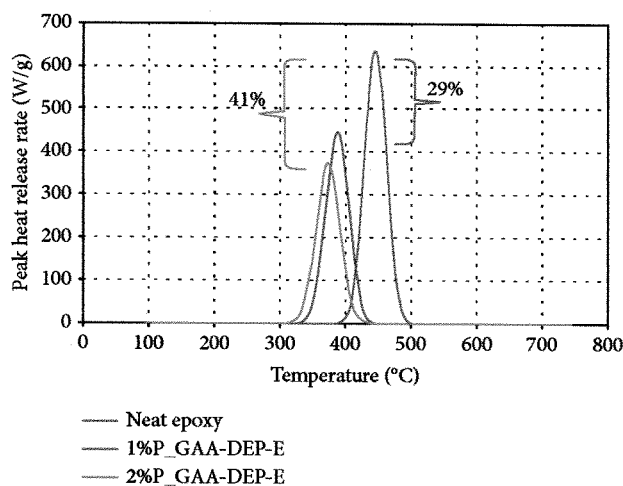


FIGURE 2: Peak heat release rates for blends of 3,4,5-tri(diethylphosphato)benzanilide with DGEBA epoxy resin.

aliquot of the reaction mixture for analysis using infrared spectroscopy. When the spectrum of the mixture no longer contained any phenolic absorption, the mixture was filtered to remove anilinium chloride which had formed. The filtrate was washed, successively, with 50 ml of water, 50 ml of 10% aqueous hydrochloric acid solution, 50 ml of 10% aqueous sodium hydroxide solution, and 50 ml of saturated aqueous sodium chloride solution. The solution was dried over anhydrous magnesium sulfate, and the solvent was removed by rotary evaporation at reduced pressure to afford 5.86 g (93.1% yield) of the triphosphate as a light tan solid: mp 79°C (DSC); ESI-MS 654 g/mol; IR (cm^{-1}) 3302 (s) N-H, 2988 (s) C_{sp^2} -H, 2912 (s) C_{sp^3} -H, 1677 (s) amide carbonyl, 1590 (m) aromatic nucleus, 1271 (s) P=O, 1013 (s) P-O-C; ^1H NMR (δ , CDCl_3) 1.35 (m, 18H, methyl protons), 4.06 (m, 4H, methylene protons), 4.28 (m, 8H, methylene protons), 7.35 (m, 7H, aromatic protons), 8.63 (s, 1H, amide proton); ^{13}C NMR (δ , CDCl_3) 15.1, 64.5, 128.4 (aromatic carbon atoms), 163.9 (carbonyl carbon atoms); ^{31}P NMR (δ , CDCl_3) 6.88, 7.20.

2.4.4. 3,4,5-Tri(dopyloxy)benzanilide. 3,4,5-Tri(dopyloxy)benzanilide was prepared in a manner similar to that described above from 5.83 g (27.1 mmol) of 9,10-dihydro-9-oxa-10-phosphaphenathrene-10-oxide (DOPO) and 1.47 g (6.0 mmol) of 3,4,5-trihydroxybenzanilide. The triester, 3,4,5-tri(dopyloxy)benzanilide (4.94 g, 93.2% yield), was obtained as a white solid: mp 187°C (DSC); ESI-MS

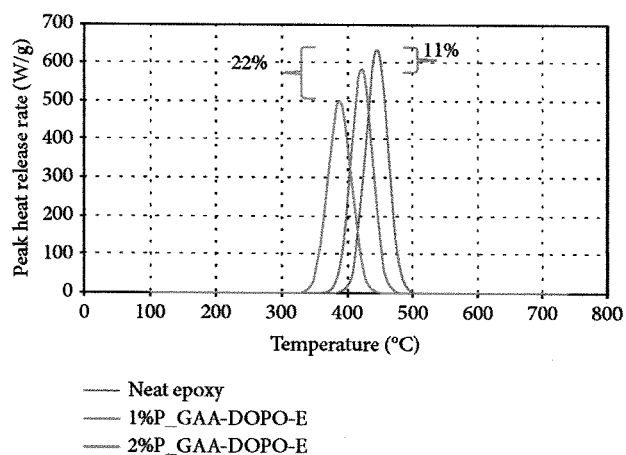


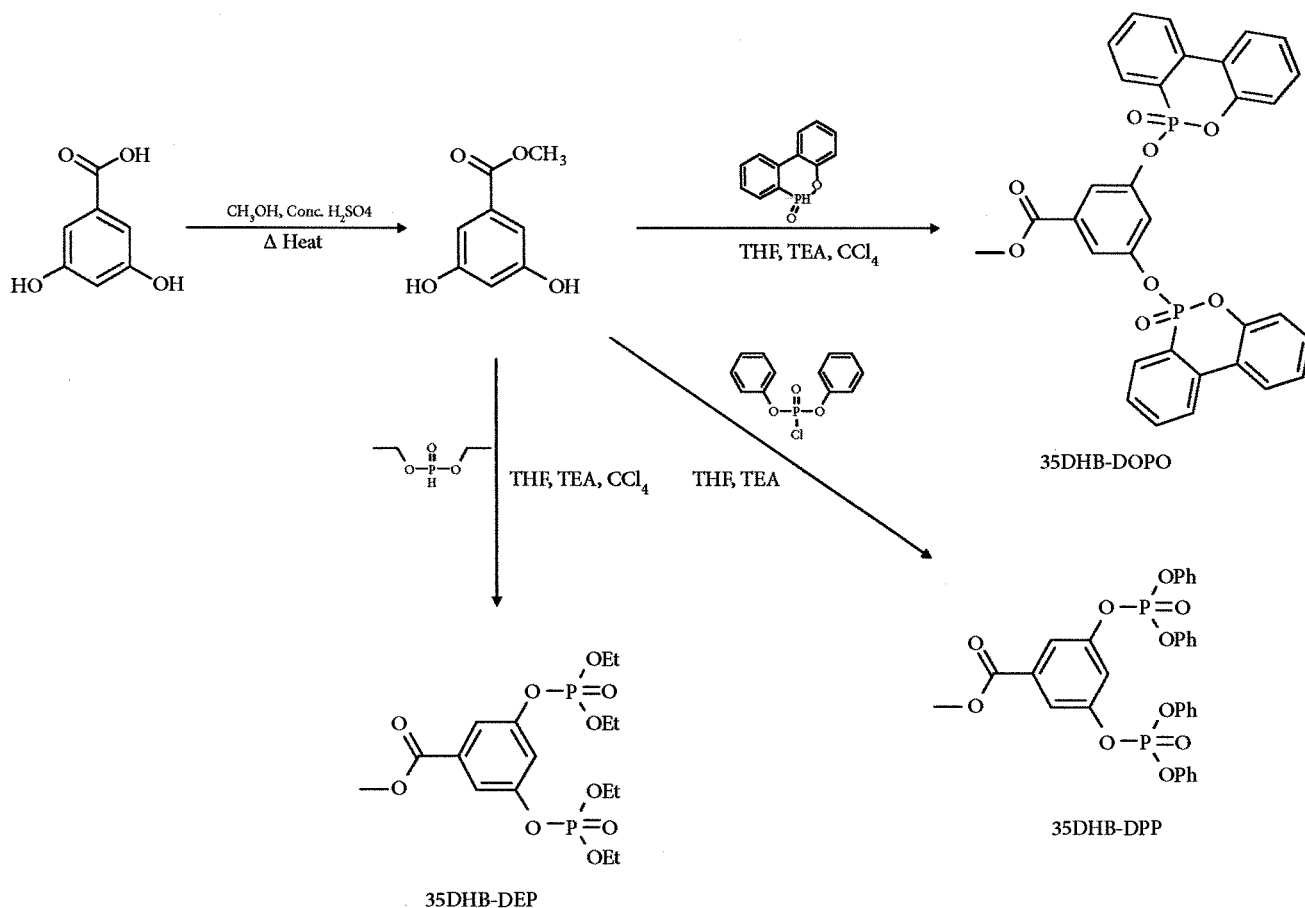
FIGURE 3: Peak heat release rates for blends of 3,4,5-tri(dopyloxy)benzanilide with DGEBA epoxy resin.

890 g/mol; IR (cm^{-1}) 3301 (w) N-H, 3066 (s) C_{sp^2} -H, 1670 (s) amide carbonyl, 1596 (s) aromatic nucleus, 1293 (s) P=O, 910 (s) P-O-C; ^1H NMR (δ , DMSO-d_6) 7.36 (m, 31H), 10.47 (s, 1H); ^{13}C NMR (δ , DMSO-d_6) 129.8 (aromatic carbon atoms), 163.0 (carbonyl carbon atom); ^{31}P NMR (δ , DMSO-d_6) 5.76, 6.63.

2.4.5. Methyl 3,5-Di(diethylphosphato)benzoate. IR (cm^{-1}) 3094 (w) C_{sp^2} -H, 2986 (m) C_{sp^3} -H, 1728 (s) ester C=O,

TABLE 4: Flammability characteristics of blends of phosphorous esters of gallic acid anilide with DGEBA epoxy resin.

Additive	Additive level (%)	Phosphorous level (%)	Peak heat release rate (W/g)	Limiting oxygen index (%)	UL 94 rating
DGEBA epoxy	0	0	692	19.0	NR
GA-DEP-E	7.5	1	491	22.5	NR
GA-DEP-E	14.0	2	411	23.0	NR
GA-DOPO-E	9.6	1	617	23.8	V2
GA-DOPO-E	19.1	2	541	27.0	V0



SCHEME 2: Synthesis of phosphorus esters of methyl 3,4-dihydroxybenzoate.

1596 (s) aromatic nucleus, 1278 (s) P=O, 1006 (s) P-O-C; ¹H NMR (δ, DMSO-d₆) 1.25 (t, J=7.1 Hz, 12H), 3.86 (s, 3H), 4.17 (q, J=7.1 Hz, 8H), 7.37 (m, 1H) and 7.61 (m, 2H) aromatic protons; ¹³C NMR (δ, DMSO-d₆) 16.3, 53.2 (ethyl carbon atoms), 117.2, 117.5, 132.8, 151.5 (aromatic carbon atoms), 164.9 (ester carbonyl carbon atom), ³¹P NMR (δ, DMSO-d₆) -7.47.

2.4.6. Methyl 3,5-Di(diphenylphosphato)benzoate. mp 68°C (DSC); IR (cm⁻¹) 3083 (w) C_{sp2}-H, 2948 (w) C_{sp3}-H, 1724 (s) ester C=O, 1588 (s) aromatic nucleus, 1300 (s) P=O, 1183 (s), 903 (s) P-O-C; ¹H NMR (δ, DMSO-d₆) 3.85 (s, 3H) 7.24-7.47 (m, 20H, protons of diphenylphosphato

groups), 7.54 (m, 1H) and 7.69 (m, 2H) (aromatic protons of trihydroxybenzoate nucleus); ¹³C NMR (δ, DMSO-d₆) 53.3 (methoxy carbon atom), 117.4, 118.4, 133.4, 150.5 (aromatic carbon atoms of trihydroxybenzoate nucleus), 116-152 (additional peaks for carbon atoms of the diphenylphosphato groups), 164.5 (ester carbonyl carbon atom); ³¹P NMR (δ, DMSO-d₆) -17.6.

2.4.7. Methyl 3,5-Di(dopyloxy)benzoate. mp 145°C (DSC); IR (cm⁻¹) 3061 (w) C_{sp2}-H, 2953 (w) C_{sp3}-H, 1731 (δ) ester C=O, 1594 (s) aromatic nucleus, 1308 (s) P=O, 1195 (s) and 929 (s) P-O-C; ¹H NMR (δ, DMSO-d₆) 3.81 (s, 3H), 6.90-8.41(m, 20H); ¹³C NMR (δ, DMSO-d₆) 53.2 (methoxy

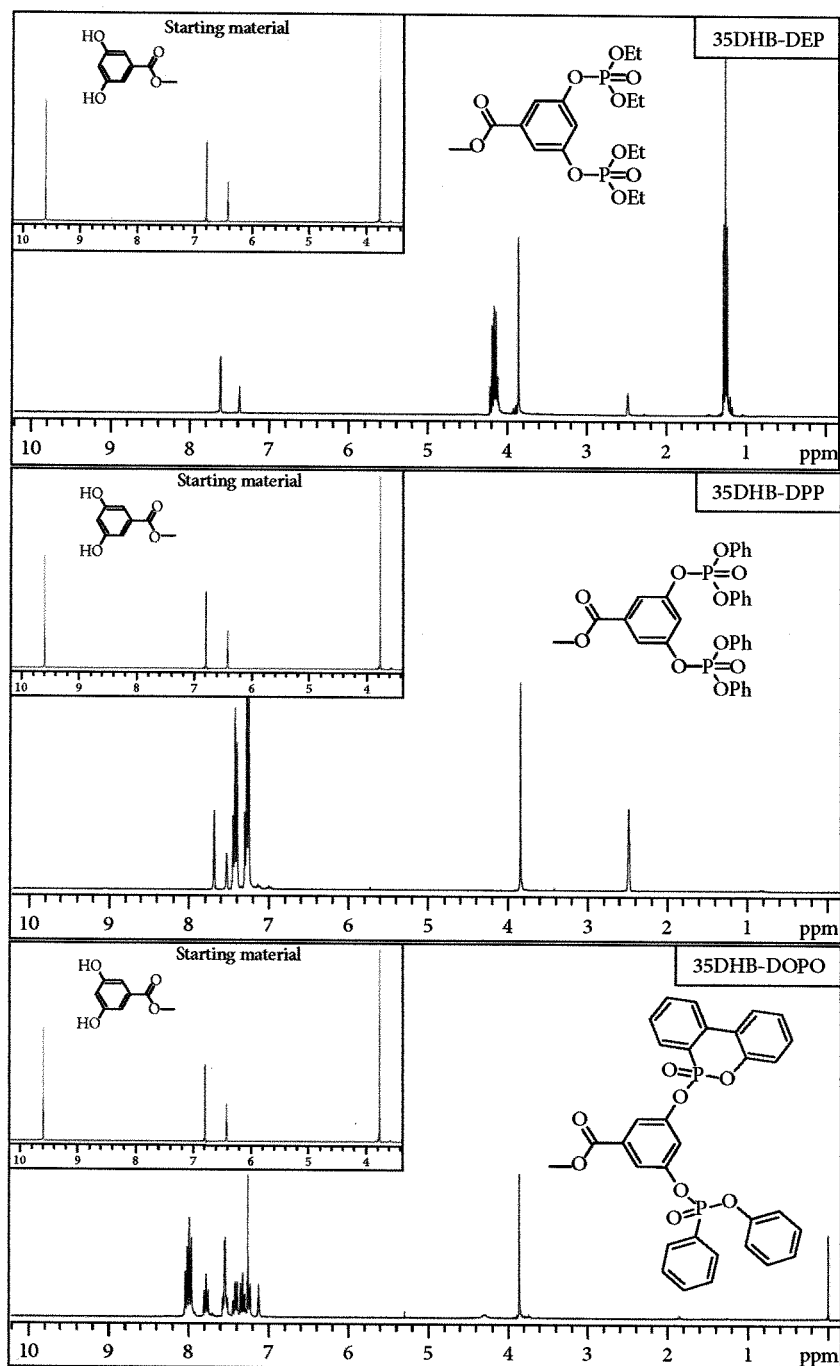


FIGURE 4: ^1H NMR spectra of phosphorus esters of methyl 3,5-dihydroxybenzoate. All the esters display good thermal stability (Table 5). Two esters, the diphenyl phosphate and the DOPO phosphonate, display decomposition onset temperatures above 300°C .

carbon atom), 116.2-151.1 (aromatic carbon atoms), 164.5 (ester carbonyl carbon atom); ^{31}P NMR (δ , $\text{DMSO}-d_6$) 6.50.

3. Results and Discussion

Gallic acid and other multihydroxybenzoic acids are found widely in nature and represent annually renewable platforms for the generation of phosphorus flame retardants. The multiple hydroxyl groups provide ready sites for the

incorporation of relatively high levels of phosphorus. The hydroxyls may be converted to a range of phosphorus esters using the well-known Atherton-Todd procedure [43]. This is illustrated in Scheme 1 for gallic acid. The acid is first converted to the corresponding anilide, and then the hydroxyls are utilized to generate both the *tris*-DOPO phosphonate and the *tris*-(diethylphosphate). Both are solids melting at 187°C and 79°C , respectively. The ^{31}P NMR spectra of both compounds contain two resonances reflecting two different

TABLE 5: Thermal decomposition of phosphorus esters of methyl 3,5-dihydroxybenzoate.

Compound	Temperature of decomposition onset (°C) ^a		Temperature of maximum decomposition rate (°C)	Decomposition residue (%) ^b	
	Nitrogen	Air		Nitrogen	Air
35DHB-DEP	224	224	272	5	<1
35DHB-DPP	328	303	366	<1	5
35DHB-DOPO	332	319	393	22	<1

^aExtrapolated onset temperature from the derivative plot of mass loss versus temperature. ^bPercentage of the initial sample mass.

environments for the phosphorus moieties. The spectrum for the *tris*-(diethylphosphate) contains peaks at $\delta = -6.88$ and -7.20 for the esters at C-4 and at C-3 and C-5, respectively. The corresponding peaks for the DOPO phosphonate appear at $\delta = 6.63$ and 7.06 . Both compounds are thermally stable to relatively high temperatures. The degradation onset temperature for the *tris*-(diethylphosphate) (GA-DEP) is 239°C , and that for the DOPO phosphonate (GA-DOPO) is 316°C . The complete decomposition characteristics are listed in Table 1.

For the assessment of flame-retarding impact, the esters were incorporated into DGEBA resin at levels sufficient to provide one and two percent phosphorus (7–19% additive). The thermal stability of the blends is reflected in Figure 1. It can be seen that the presence of the phosphorus esters does not significantly lower the thermal stability of the epoxy polymer. Numerical data for the degradation of the phosphorus ester/epoxy blends are collected in Table 2.

Glass transition temperatures for the phosphorus ester blends with epoxy are collected in Table 3. As may be seen, the glass transition temperature for the resin is altered only slightly by the presence of the esters.

The flammability of the blends was assessed using limiting oxygen index (LOI) measurements, UL 94 vertical burn test, and microscale combustion calorimetry (MCC). Plots for the peak heat release rates for blends of 3,4,5-tri(diethylphosphato)benzanilide in epoxy are displayed in Figure 2, and those for the analogous DOPO ester blends in Figure 3. In both cases, a significant peak heat release rate reduction for the combustion of epoxy is achieved by incorporation of either of the phosphorus esters at a level sufficient to provide one or two percent phosphorus. This is particularly true for the incorporation of 3,4,5-tri(diethylphosphato)benzanilide.

All the flammability data are collected in Table 4. Most notably, incorporation of two percent 3,4,5-tri(dopyloxy)benzanilide into DGEBA epoxy afforded a material with a 22% peak heat release rate reduction, an LOI value of 27, and a UL 94 rating of V0.

The preparation of phosphorus esters of methyl 3,5-dihydroxybenzoate is illustrated in Scheme 2. The progress of the reaction may conveniently be monitored using infrared spectroscopy. The band for hydroxyl absorption (3229 cm^{-1}) in the spectrum of the starting material gradually disappears. The spectra for the phosphorus esters contain prominent absorptions for ester carbonyl (1728 , 1724 , and 1731 cm^{-1}), aromatic nuclei (1596 , 1588 , and 1594 cm^{-1}), P=O (1278 , 1300 , and 1308 cm^{-1}), and P-O-C (1006 , 1183 , 903 , 1185 ,

TABLE 6: Glass transition temperatures for blends of phosphorus esters of methyl 3,5-dihydroxybenzoate with DGEBA epoxy resin.

Additive	Additive level (wt%)	Phosphorus level (wt%)	T_g (°C)
None	0	0	109
35DHB-DEP	7.1	1	126
35DHB-DEP	14.2	2	137
35DHB-DPP	10.2	1	119
35DHB-DPP	20.4	2	116
35DHB-DOPO	9.6	1	128
35DHB-DOPO	19.2	2	142

and 929 cm^{-1}). The proton NMR spectra for the phosphorus esters may be found in Figure 4. All contain distinct absorptions for the aromatic nucleus of the starting material as well as those expected for the ester moieties.

For the assessment of the impact of these esters on flammability, blends of these esters at a level to provide one or two percent phosphorus with DGEBA epoxy were prepared. As may be seen from the data presented in Table 6, the incorporation of the esters at these levels does not appreciably alter the glass transition temperature for the polymer. The thermal stability for the blends is reflected in Table 7. The thermal stability of the resin is not much impacted by low loadings of the esters.

The peak heat release rates for blends of the esters with DGEBA epoxy are shown in Figures 5-7. The reduction in peak heat release is most notable for the *bis*-diethylphosphato ester. For this compound, a loading sufficient to provide 2% phosphorus induces a 50% reduction in the peak heat release rate.

Flammability data for all the blends are collected in Table 8. The most effective compound is the di(dopyloxy) ester. At a loading sufficient to provide 2% phosphorus, combustion of the blend reflects a reduction in the peak heat release rate (678 W/g to 519 W/g), an LOI of 33, and a UL 94 rating of V2.

For both series of phosphorus esters, their incorporation into DGEBA epoxy resin at levels sufficient to provide one or two percent phosphorus does not significantly impact the properties or thermal stability of the polymer but does impart significant flame retardancy. The DOPO phosphonate is the most effective. This is clear from both LOI and UL 94

TABLE 7: Thermal degradation characteristics for blends of phosphorus esters of methyl 3,5-dihydroxybenzoate in DGEBA epoxy resin.

Additive	Additive level (wt%)	Phosphorus level (wt%)	T_{onset} ($^{\circ}\text{C}$) ^a	T_{max} ($^{\circ}\text{C}$) ^b	Char ^c (wt%)
None	0	0	390	423	10
35DHB-DEP	7.1	1	345	373	23
35DHB-DEP	14.2	2	329	355	26
35DHB-DPP	10.2	1	349	375	24
35DHB-DPP	20.4	2	328	356	27
35DHB-DOPO	9.6	1	369	394	15
35DHB-DOPO	19.2	2	354	379	18

^aExtrapolated onset temperature from the derivative plot of mass loss versus temperature. ^bPercentage of the initial sample mass. ^cNitrogen atmosphere.

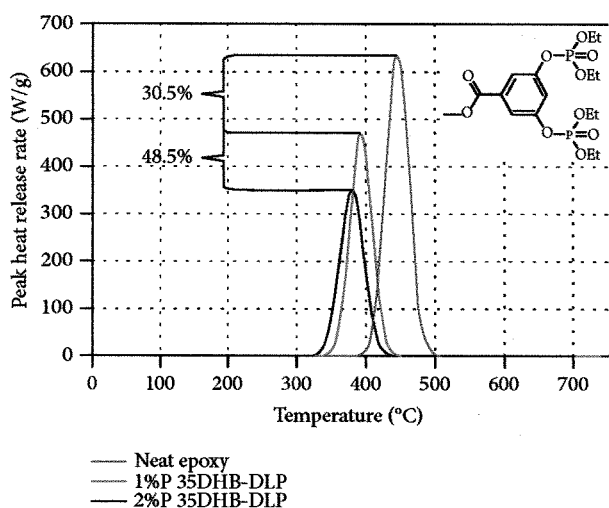


FIGURE 5: Peak heat release rates for blends of methyl 3,5-di(diethylphosphato)benzoate in DGEBA epoxy.

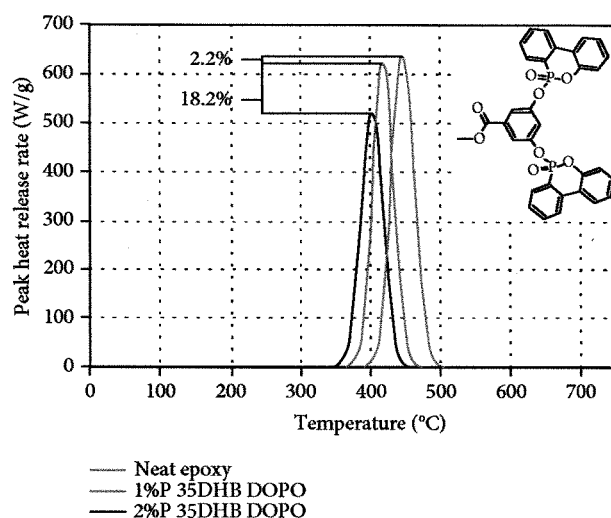


FIGURE 7: Peak heat release rates for blends of methyl 3,5-di(doplyoxy)benzoate in DGEBA epoxy.

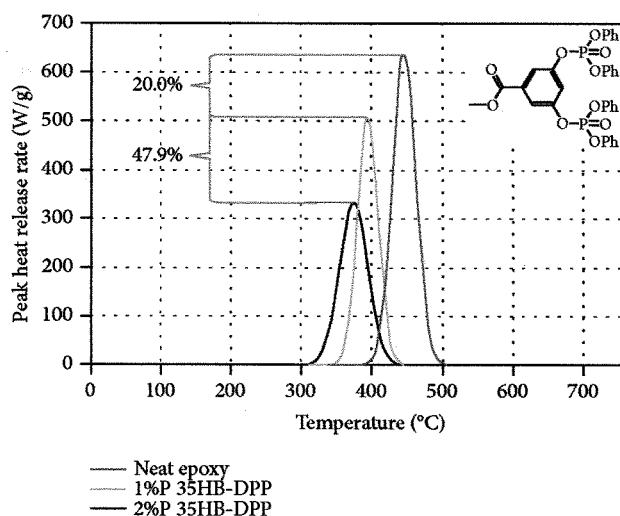


FIGURE 6: Peak heat release rates for blends of methyl 3,5-di(diphenylphosphato)benzoate in DGEBA epoxy.

measurements. The phosphates promote char formation and strongly lower the peak release rate for the combustion of the polymer. The peak heat release rate reduction for the

polymer containing the DOPO phosphonate is much smaller than that for the polymer containing the corresponding phosphates. This is probably reflective of the different modes of action. DOPO derivatives are generally thought to act predominately by liberating species to the gas phase which inhibits flame-propagating reactions [44, 45]. The results from MCC may underestimate the effectiveness of flame retardants that function in the gas phase [46–48]. The action of a phosphorus ester additive is dependent on the level of oxygenation at phosphorus [49–52]. In general, increasing gas phase activity is observed for a decreasing level of oxygenation at phosphorus [48–51]. Compounds with a high level of oxygenation at phosphorus tend to promote char formation in the solid phase. These observations are consistent with those presented here. It would appear that the phosphates function largely in the solid phase while the phosphonates display predominately gas phase activity.

4. Conclusions

Gallic acid and other multihydroxybenzoic acids are found widely in nature and represent a renewable biosource for the generation of effective phosphorus flame retardants. Gallic acid and 3,5-dihydroxybenzoic acid have been

TABLE 8: Flammability characteristics for blends of phosphorus esters of methyl 3,5-dihydroxybenzoate with DGEBA epoxy.

Compound	% phosphorus	PHRR (W/g)	THR (kJ/g)	LOI (% O ₂)	UL 94 rating	% additive
Epoxy	0%	677.7	29.8	19	NR	0
35DHB-DEP	1%	470.9	25.7	23.6	NR	7.1
	2%	348.7	18.9	23.4	NR	14.2
35DHB-DPP	1%	505.4	23.3	24.6	NR	10.2
	2%	330.1	20.1	24.6	NR	20.4
35DHB-DOPO	1%	620.3	22.5	30.8	NR	9.6
	2%	518.8	22.6	33.3	V2	19.2

converted to a series of phosphorus esters that display good flame retardancy in DGEBA epoxy resin. Phosphonates have a greater inhibitory effect on the flammability of the resin than do the corresponding phosphates and probably function predominately in the gas phase.

Data Availability

Structural and flammability data used to support the findings of this study are included within the article.

Conflicts of Interest

The authors declare that there is no conflict of interest regarding the publication of this paper.

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