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1-Dopyl-1,2-(4-hydroxyphenyl)ethene: A flame retardant hardner for epoxy resin

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ABSTRACT

Treatment of desoxyanisoin with 9,10-dihydro-9-oxaphosphaphenathrene-10-oxide (DOPO) in the presence of an acid catalyst generates an adduct, 1-dopyl-1,2-(4-methoxyphenyl)ethene which may be readily converted to the corresponding diphenolic compound, 1-dopyl-1,2-(4-hydroxyphenyl)ethene (BDE). This material behaves as an effective curing agent for the diglycidyl ether of bisphenol A (DGEBA) to provide a thermally stable (T_{dec} 417 °C) resin with Tg of 146 °C. This polymer displays outstanding flammability characteristics – an LOI of 36 (compared to 19 for conventionally cured resin), a total heat release of 20 kJ/g and a UL 94 V0 rating. The flame retardant impact of the incorporation of this hardner into the resin is due both to its structure (promotes char formation for solid phase activity) and the presence of the DOPO substituent (promotes gas-phase activity).

1. Introduction

Epoxy resins are important materials utilized in a wide rage of applications, most notably in electronics. They possess numerous positive characteristics including outstanding electrical and mechanical properties [1,2]. A major liability for the use of these materials is ready flammability. For use, they must be flame retarded. Traditionally, a reduction in flammability has been achieved through incorporation of brominated compounds, most notably tetrabromobisphenol A. Although, organohalogen compounds are quite effective as flame retardants, they may be converted to toxic dioxins during combustion of the polymer [3,4]. A more prominent problem is the release of these materials from the polymer matrix into the surroundings, particularly upon degradation in a landfill [5,6]. This leads to environmental contamination and human exposure which can give rise to the numerous disease states, most associated with endocrine disruption [7]. For this reason, the use of these compounds is being widely restricted by both governmental regulation and societal lack of acceptance [8,9]. The development of organophosphorus compounds as replacements for offending organohalogen materials is occurring rapidly [10,12]. Many of these have been derivatives of 9,10-dihydro-9-oxaphosphaphenanthrene-10-oxide (DOPO) [13–16]. These may be incorporated as discrete compounds, or as substituents on the epoxy monomer or often as components of the curing agent (hardner) [17–24]. Various nucleophilic compounds including most prominently diamines but also diphenolics, mercaptans, anhydrides and others have been utilized for the curing of epoxy [25]. Of particular note are the imidazoles which function as effective curing agents at relatively low temperature [26,27]. Among these, 2-ethyl-4-methylimidazole (EMI) is widely used for curing epoxy for the electronics industry and is a convenient hardner for the preparation of laboratory samples [28]. In this case, a flame retardant hardner has been prepared by treating desoxyanisoin with DOPO followed by acid catalyzed removal of the methyl groups to generate 1-dopyl-1,2-(4-hydroxyphenyl)ethene (BDE). This hardner is unique in that it possesses a structure known to facilitate char formation and one containing a dopyl substituent.

2. Experimental

2.1. Materials

Common solvents are reagents were from commercial sources, most often ThermoFisher Scientific or Sigma-Aldrich, and purified as appropriate [28]. Desoxyanisoin was obtained from Alfa Aeser. The diglycidyl ether of biphenol A (DGEBA) was supplied by the Dow Chemical Company.

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2.2. Methods

In general, reactions were carried out in a dry (all glassware was dried at 120 °C and allowed to cool under a stream of dry nitrogen prior to use) three-necked, round-bottomed blask fitted with a Liebig condenser bearing a gas-inlet tube, a pressure-equalizing dropping funnel or thermometer, and a magnetic stirring bar. Thin layer chromatography (TLC) was performed using silica coated Mylar plates (ThermoFisher Scientific). Chromatography was accomplished using SilaFlash P60 (230–400 mesh silica; Silicycle) in a column of appropriate size and hexane/ethyl acetate as a eluent. Final purification was by crystallization from ethyl acetate/hexane.

2.3. Synthesis

2.3.1. 1-Dopyl-1,2-(4-methoxyphenyl)ethene

A mixture of 25.01 g (97.5 mmol) of desoxyanisoin, 1.86 g (9.78 mmol) of *p*-toluensulfonic acid and 42.17 g (19.5 mmol) of DOPO was stirred at 150 °C for 5 h. The mixture was allowed to cool and diluted with 800 ml of ethyl acetate. The solution was washed, successively, with three 100-ml portions of saturated aqueous sodium bicarbonate solution and 100 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 provide a crude product as a faintly-colored solid. Analysis of this material by TLC indicated that it was a mixture of four compounds, one major and three minor. Two of these appeared to be isomeric (very similar retention values). Analysis by mass spectrometry confirmed this observation. The major component had a molar mass of 454 g/mol, a first minor component has a molar mass of 472 g/mol (a difference of water from the mass of the major component) and the two isomeric components a molar mass of 670 g/mol reflecting the addition of two DOPO units. The crude material was subjected to column chromagraphy (silica gel; ethyl acetate/hexane, 1/10) to provide 21.0 g (47.1% yield) of 1-dopyl-1,2-(4-methoxyphenyl)ethene as a white solid. Recrystallization from ethyl acetate/hexane provided analytically pure, X-ray quality crystals: mp 183 °C (DSC); ESI-MS 455 g/mol $[M+H]^+$; FTIR (ATR, cm^{-1}) 3058 (vw), 3042 (w), 3015 (vw) C_{sp2}-H, 2956 (w), 2930 (w), 2905 (vw) C_{sp3}-H, 1601 (vs), 1508 (vs) aromatic nucleus, 1286 (m) P=O, 1236 (vs) 1176 (vs) C–O; ^{1}H NMR (δ, $CDCl_3$) 3.69 (s, 3H, methyl protons), 3.74 (s, 3H, methyl protons), 6.67–7.86 (vinyl and aromatic protons); ^{13}C NMR (δ, $CDCl_3$) 55.2, 55.3 (methyl carbon atoms), 113.9, 114.4 (vinyl carbon atoms), 120.3–160.6 (aromatic carbon atoms); ^{31}P NMR (δ, $CDCl_3$) 24.5.

2.3.2. 1-Dopyl-1,2-(4-hydroxyphenyl)ethene (BDE)

A mixture of 21.02 g (46.2 mmol) of 1-dopyl-1,2-(4-methoxyphenyl)ethene and 21.3 g (19.0 mmol) of pyridinum chloride was stirred at 190 °C for 6 h [29,30]. The mixture was poured into 1000 ml of rapidly stirred water. Stirring was maintained for several hours. The precipitate which had formed was collected by filtration at reduced pressure and recrystallized from methanol to provide 10.2 g (52.2% yield) of 1-dopyl-1,2-(4-hydroxyphenyl)ethene as a white solid: mp.

295 °C (DSC); ESI-MS 427 g/mol $[M+H]^+$; FTIR (ATR, cm^{-1}) 3190 (s) O–H, 3060 (m) C_{sp2}-H, 1595 (vs), 1510 (s) aromatic nucleus, 1267 (m) P=O, 1191(vs), 116 (vs) C–O; ^{1}H NMR (δ, DMSO-d_6) 6.59–8.12 (17H, vinyl and aromatic protons), 9.47 (1H, phenolic proton), 9.96 (1H, phenolic proton); ^{13}C NMR (δ, DMSO-d_6) 115.3, 115.8 (vinyl carbon atoms), 119.9–159.0 (aromatic carbon atoms); ^{31}P NMR (δ, DMSO-d_6) 23.5.

2.4. Characterization

Infrared (IR) spectra were obtained using attenuated total reflectance and a ThermoScientific Nicolet iS 50 FTIR Spectrometer. Absorptions were recorded in wavenumbers (cm^{-1}) and absorption intensities were classified as very weak (vw), weak (w), medium (m), strong (s), and very strong (vs) relative to the intensity of the strongest band in the spectrum. Nuclear magnetic resonance (NMR) spectra were obtained using a Varian Mercury 300 MHz or Inova 500 MHz spectrometer and 5–25% solutions in deuterochloroform or dimethyl sulfoxide-d_6. ^{1}H and ^{13}C chemical shifts are reported in parts-per-million (δ) with respect to the resonance for tetramethylsilance (TMS) as internal reference ($\delta = 0.00$). ^{31}P NMR spectra were similarly recorded using triphenyl phosphate ($\delta = -18.00$) an internal reference. Mass spectra were obtained using a Waters Aquilty/LCT Premier XE electrospray ionization mass spectrometer with samples introduced as dilute solutions in acetonitrile/water. Thermal transitions were determined using differential scanning calorimetry (DSC) and a TA Instruments Q 2000 unit. Samples, contained in standard aluminum pans, were analyzed at a heating rate of 5 °C/min. Curing of DGEBA with DBE was monitored using DSC to determine the optimum ratio of reactants to achieve full cure. Thermal stability was determined using a TA Instruments Q500 thermogravimetric analyzer and a heating rate of 10 °C/min. Samples (5–10 mg) were contained in a platinum pan. The sample compartment was purged with dry nitrogen at 50 ml/min during analysis. X-ray crystallographic analysis was carried out in the Instrumentation Facility, University of Toledo (details may be found in Supporting Material).

2.5. Sample preparation

Appropriate amounts of DGEBA and DBE (to achieve the desired ratio of functional groups) were placed in a 50-ml beaker and stirred at 110 °C until homogenous. Aliquots of the material was removed for examination using DSC and the bulk was transferred to preheated Teflon molds. The molds were placed in an oven and held at 175 °C for 1 h. The temperature was then increased and held at 200 °C for 6 h. The samples were allowed to cool slowly (over a period of approximately 12 h) to provide plaques for characterization and flammability testing. Plaques of 3 x 13 × 130 mm were obtained and used for both LOI and UL 94 testing.

2.6. Flammability testing

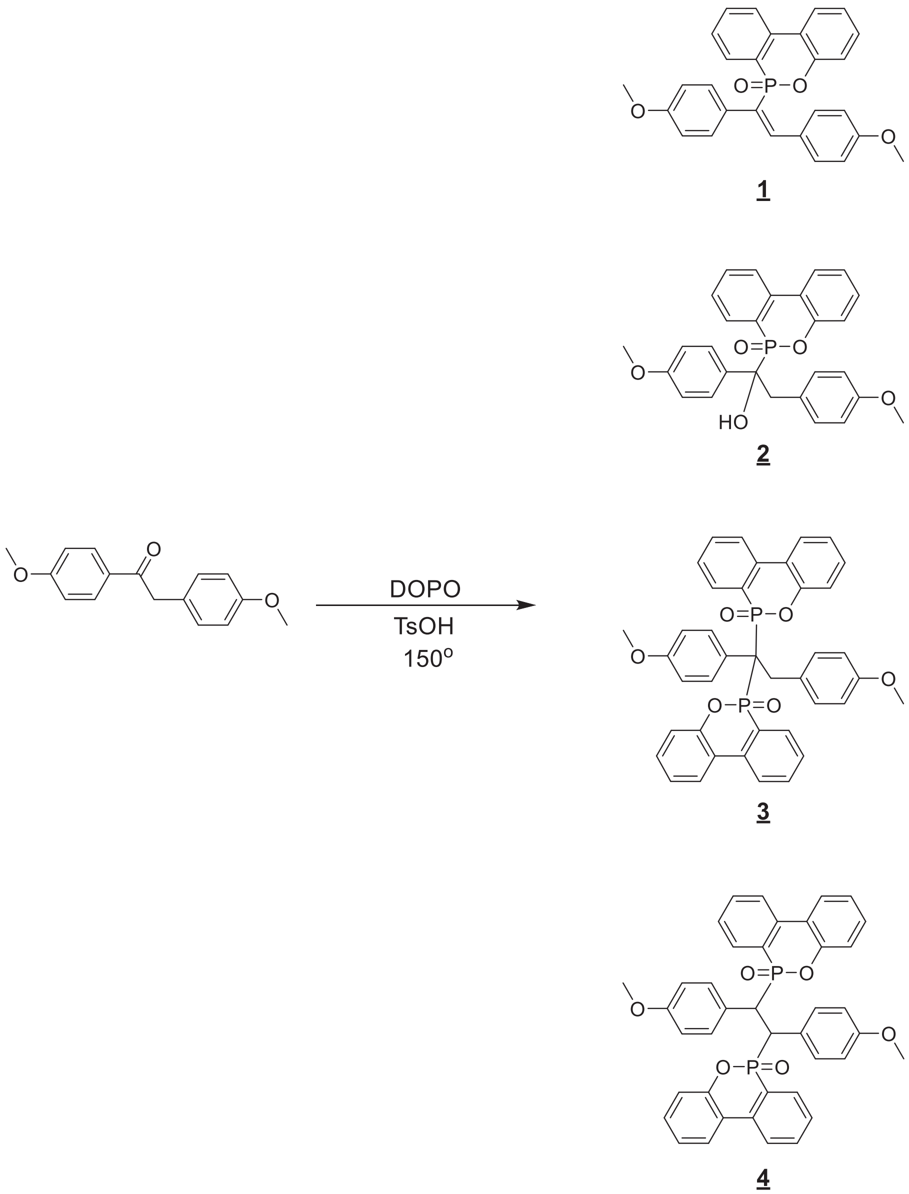
The flammability characteristics of epoxy cured with DBE were assessed as previously described using standard laboratory scale techniques: limiting oxygen index (LOI; ASTM D2863-13), the UL 94 vertical burn test (ASTM D568), and microscale combustion calorimetry (MCC; ASTM D7309-07a) [31,32].

3. Results and discussion

Flame retarding epoxy resin while avoiding the use of organohalogen compounds is being vigorously pursued [10–24]. Organophosphorus compounds, particularly DOPO derivatives, introduced in a variety of ways have been particularly effective. 4,4-Bishydroxydeoxybenzoin is readily available from desoxyanisoin by acidolysis and has been used for the generation of a variety of flame resistant or flame retardant polymeric materials [33–37]. Treatment of desoxyanisoin with DOPO in the presence of an acid catalyst generates a mixture of addition products. Analysis of the mixture using TLC indicated that it contained a single major product and three minor products, two of which appeared to be isomeric (very similar retention values). Analysis of the mixture using ESI-MS confirmed this observation and provided structural information. The major component has a molar mass of 454 g/mol consistent with the composition of 1-dopyl-1,2-(4-methoxyphenyl)ethene **(1).** A first minor component has a molar mass of 472 g/mol (a difference of the elements of water from the mass of the major component) which is consistent with the structure for the initial DOPO adduct, 1-dopyl-1,2-(4-methoxyphenyl)ethanol **(2).** The two isomeric compounds have molar mass of 670 g/mol reflecting the addition of two DOPO units and were identified as 1,1-didopyl-1,2-(4-methoxyphenyl) ethene **(3)** and 1,2-didopyl-1,2-(4-methoxyphenyl)ethene **(4)**, respectively. The formation of these products is reminiscent of the previously reported addition of DOPO to ketones [38]. The overall transformation is shown in Scheme 1. The major product, 1-dopyl-1,2-(4-methoxyphenyl)ethene, was isolated by chromatography and recrystallized from hexane/ethyl acetate (90:10) to afford a sharply melting white solid, 181 °C (DSC). The structure for this compound was rigorously established using spectroscopic and X-ray crystallographic techniques. The infrared spectrum for this compound is shown in Fig. 1.

Prominent peaks appear at 1601 and 1508 cm^{-1} (aromatic nuclei), 1286 cm^{-1} (P═O) and 1236, 1176 cm^{-1} (C–O). Proton and ^{13}C NMR spectra are displayed in Fig. 2. The proton spectrum contains resonances for the methoxy protons at δ 3.69 and 3.74 as well as resonances for vinyl and aromatic protons in the region δ 6.67–7.86. The ^{13}C spectrum contains resonances for the methoxy carbon atoms, δ 55.2 and 55.3, vinylic carbon atoms, δ 113.9, 114.4, as well as aromatic carbon atoms. A resonance for a carbonyl carbon atom is not present. The ^{31}P spectrum contains a single sharp peak at δ 24.5. The structure as determined by X–ray crystallography is depicted in Fig. 3 (all data may be found in Supplemental Material). This structure confirms the placement of the dopyl unit at a carbon-carbon double bond (bond distance of 1.347 Å). 1-Dopyl-1,2-(4-methoxyphenyl)ethene was converted to the corresponding diphenol, 1-dopyl-1,2-(4-hydroxyphenyl)ethene (BDE) by treatment with pyridinium chloride (Scheme 2). BDE is a sharply melting (295 °C) white solid.

The infrared spectrum shown in Fig. 4 contains broad hydroxyl absorption centered at 3190 cm^{-1}, aromatic absorption at 1595,



Scheme 1. Reaction of DOPO with Desoxyanisoin.

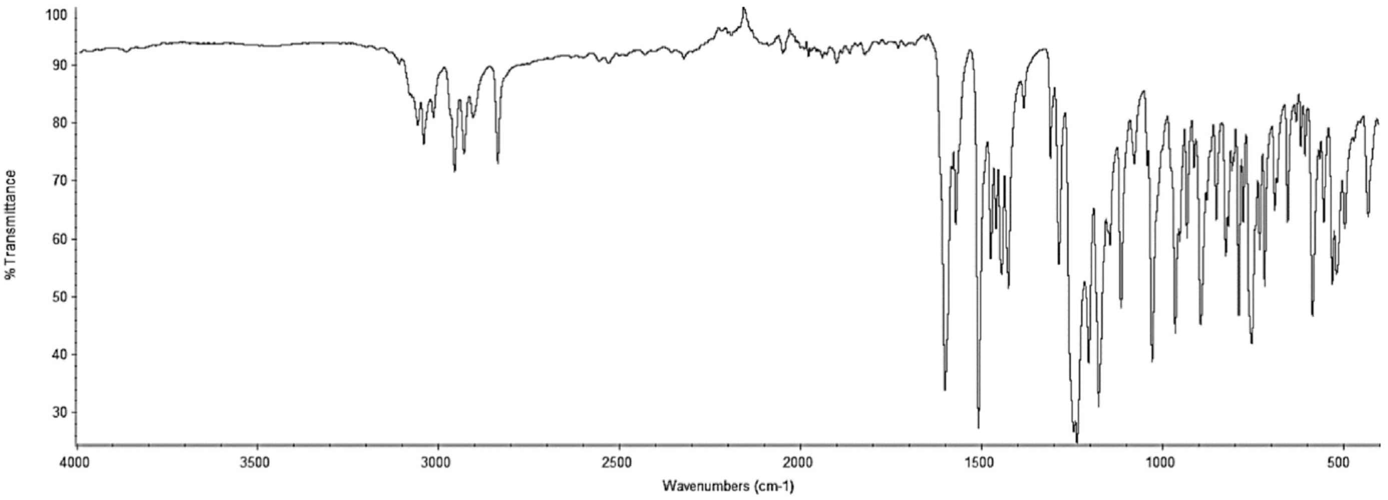


Fig. 1. Infrared spectrum for 1-dopyl-1,2-(4-methoxyphenyl)ethene.

1510 cm^{-1}, absorption for a P–O double bond at 1267 cm^{-1} and C–O absorption at 1191 and 1166 cm^{-1}. Proton and ^{13}C NMR spectra for this compound are contained in Fig. 5.

The proton spectrum contains resonances for vinyl and aromatic protons, δ 6.59–8.12, and for phenolic protons at δ 9.47 and 9.96. The ^{13}C spectrum contains resonances for vinyl carbon atoms at δ 115.3 and 115.8 as well as those for aromatic carbon atoms, δ 119.9–159.0. The ^{31}P spectrum contains a single sharp resonance at δ 23.5.

The curing of DGEBA with BDE was initially explored using DSC. Curing was clearly apparent from an exotherm with an onset of about 165 °C. The extent of cure increased as the ratio of BDE to DGEBA increased. Cure was complete for a mixture containing 50 mol% BDE, i.e., for a mixture containing an equimolar concentration of phenolic and epoxy groups. The glass transition temperature (Fig. 6) for the material undergoing curing increased to a maximum of 146 °C for the fully cured epoxy. The thermal stability of both partially and fully cured resin is reflected in Fig. 7. The plots of mass loss versus temperature for the partially cured samples reflect

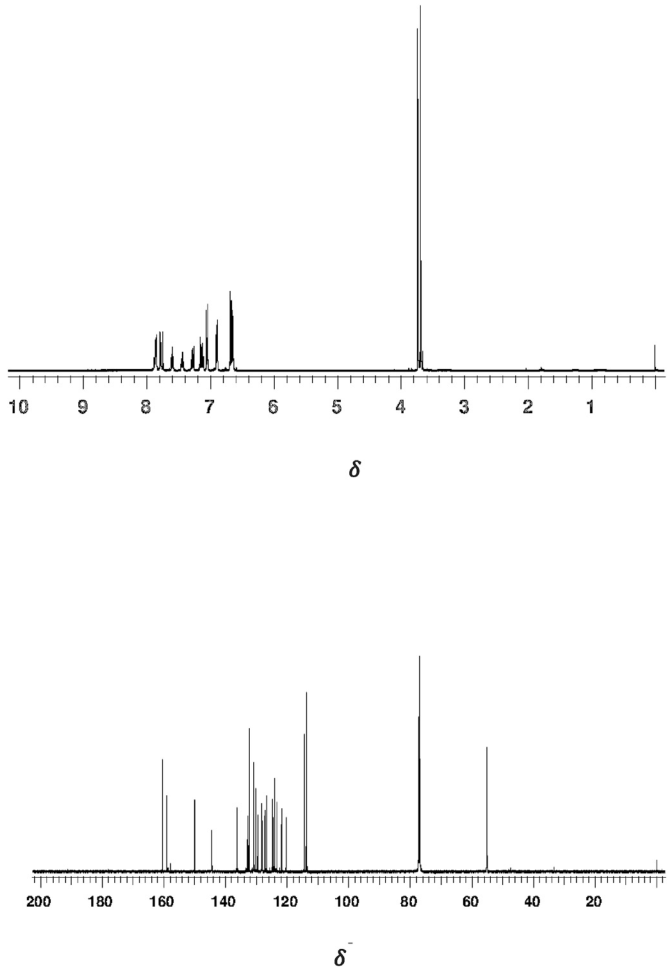


Fig. 2. Proton and Carbon-13 NMR spectra for 1-dopyl-1,2-(4-methoxyphenyl)ethene.

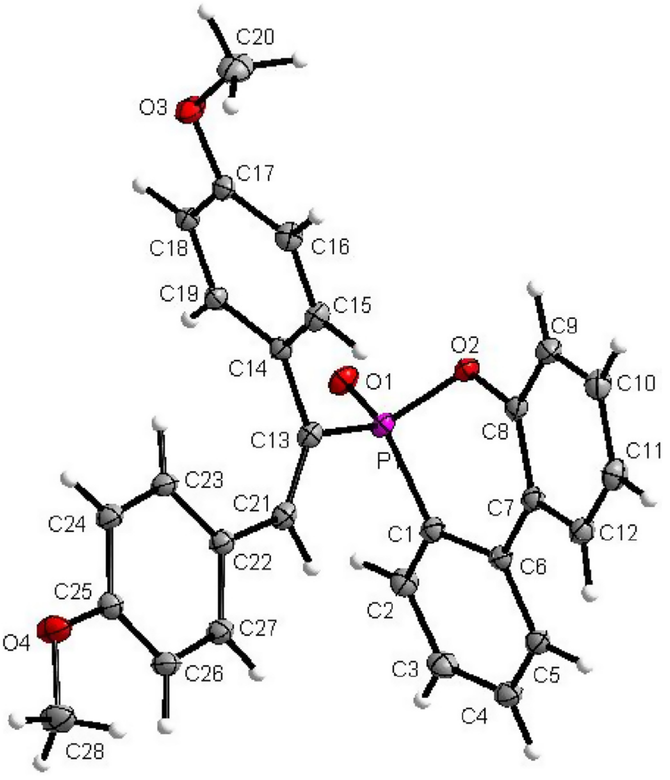
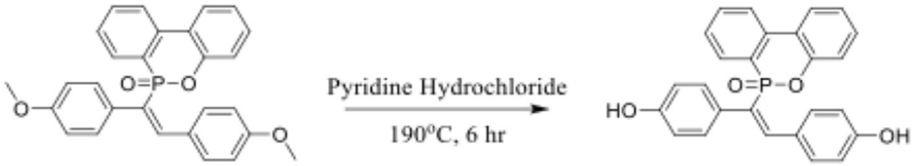


Fig. 3. Depiction of the Crystal Structure of 1-Dopyl-1,2-(4 methoxyphenyl)ethene.



Scheme 2. Conversion of 1-Dopyl-1,2-(4-methoxyphenyl)ethene to 1-Dopyl-1,2-(4hydroxyphenyl)ethene (BDE).

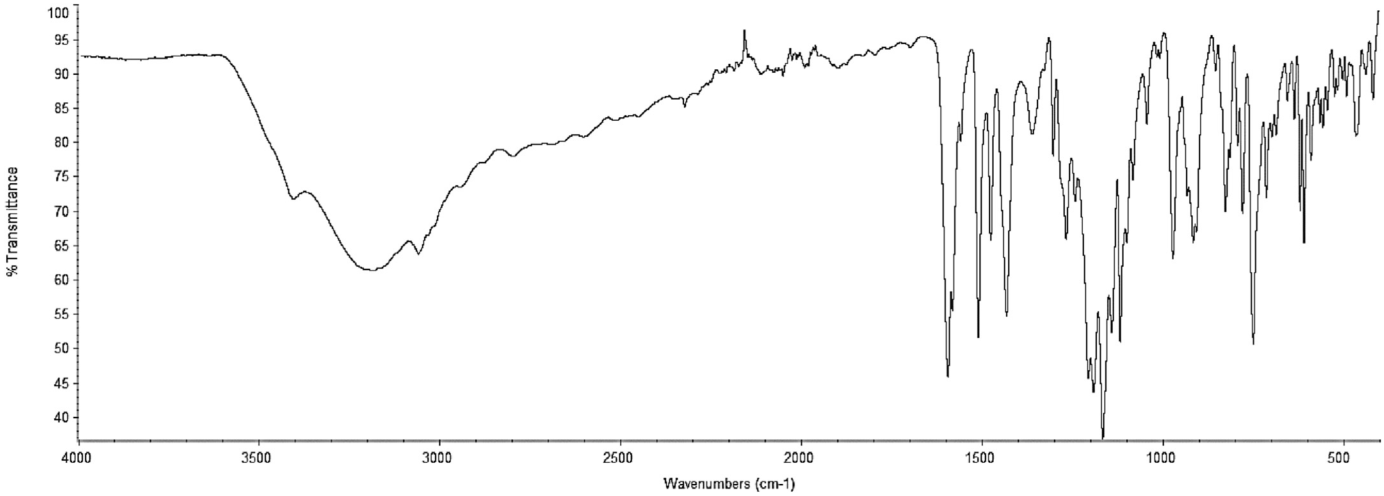


Fig. 4. Infrared spectrum for 1-dopyl-1,2-(4-hydroxyphenyl)ethene (BDE).

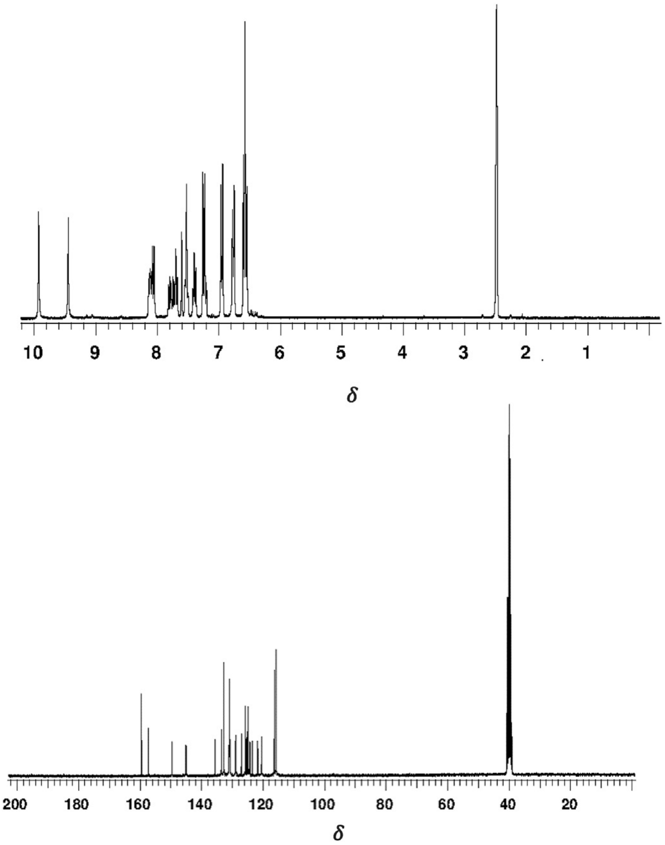


Fig. 5. Proton and Carbon-13 NMR spectra for 1-dopyl-1,2-(4-hydroxyphenyl)ethene (BDE).

an early loss of unchanged epoxy. This loss is not present in the plot for the fully cured sample. It should be noted that the thermal decomposition of the fully cured sample generates a char residue (700 °C) that represents 26% of the initial sample mass. Clearly, the presence of phosphorus-containing curing agent promotes char formation. The flammability of the fully cured sample was evaluated and compared to that for resin generated using a conventional amine curing agent, 2-ethyl-4-methylimidazole. The results are presented in Table 1. Several observations are apparent. First, incorporation of 4% phosphorus, *via* the hardner, into the resin is quite effective in reducing flammability. The LOI of 36 is double that for the conventionally cured resin containing no flame retardant. This unusual effectiveness is also reflected in the total heat release (20 kJ/g) which is nearly half that for the imidazole cured resin. The large amount of residue remaining after pyrolysis (26%, almost identical to that observed by thermogravimetry) may be reflective of the structure of BDE. It has been suggested that the unusual effectiveness of deoxybenzoin derivatives in flammability reduction arises from ready conversion to acetylene derivatives which may cyclize and lead to char formation [36]. Elimination of DOPO from BDE would generate an acetylene derivative that could promote char formation (Scheme 3). This might also be reflected the peak heat release rate (704 W/g) which is nearly the same as that for the resin cured with a conventional curing agent. It is known that DOPO decomposes to liberate PO radical to the gas phase where it effectively scavenges combustion propagating radicals [39,40]. Further, MCC tends to underestimate the effectiveness of flame retardants that function primarily in the gas phase [41–44].

4. Conclusions

A phosphorus-contaning diphenolic hardner for expoxy has

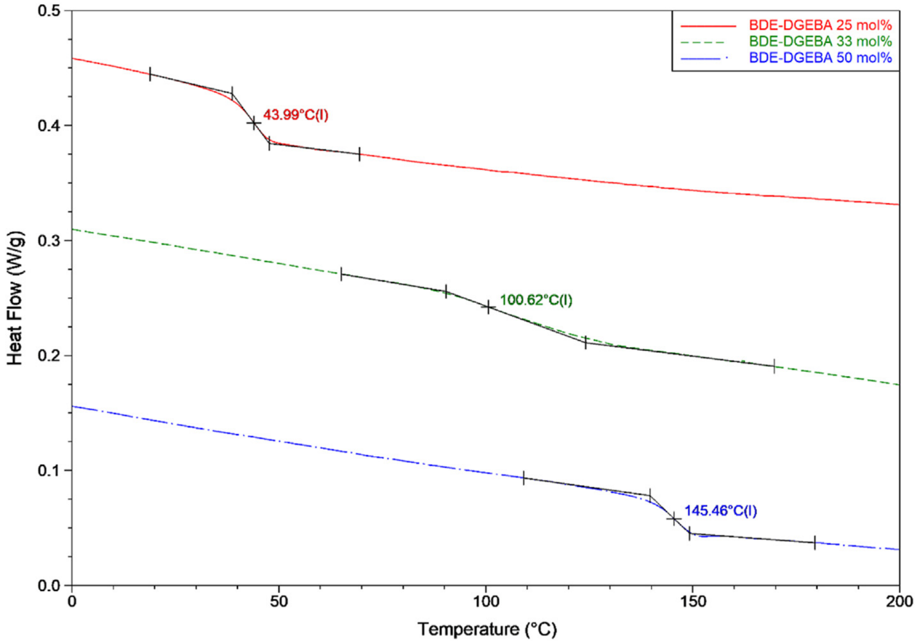


Fig. 6. Glass transition temperatures for DGEBA partially and fully cured with BDE.

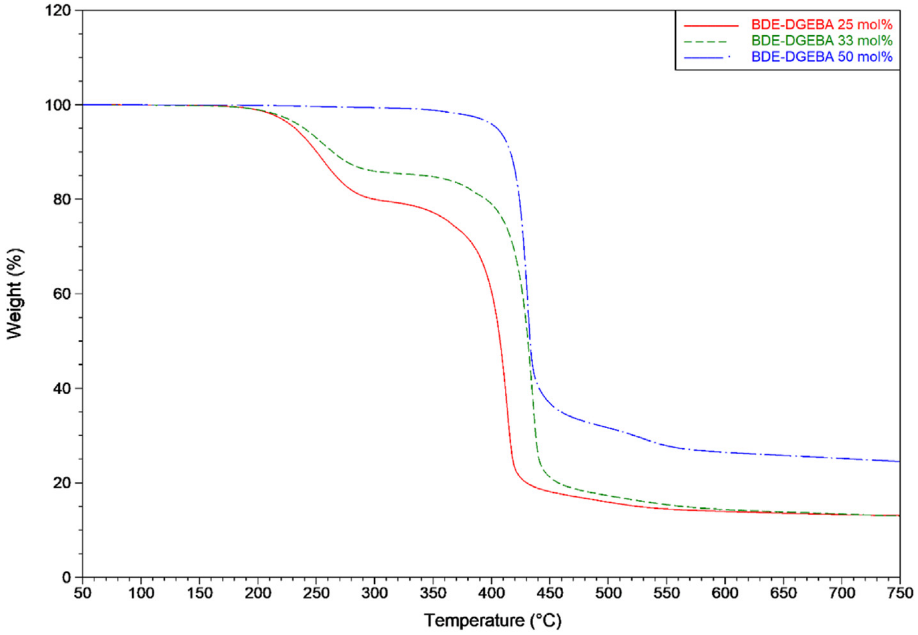
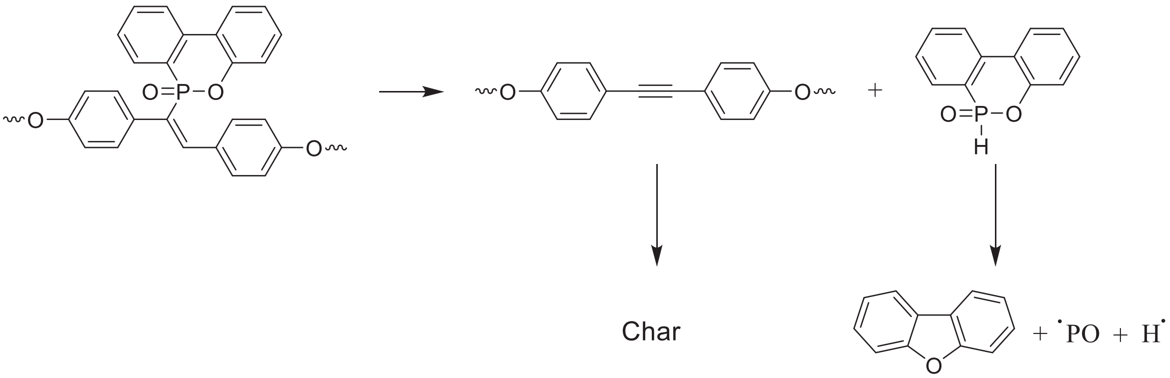


Fig. 7. Thermal stability of DGEBA partially and fully cured with BDE.

Table 1
Comparison of flammability properties of epoxy resin cured with 2-ethyl-4-methylimidozole (EMI) and that cured with 1-dopyl-1,2-(4-hydroxyphenyl)ethene (BDE).

Curing Agent	%P (Mass)	LOI	UL 94 Rating	PHRR[a] (W/g)	THR[a] kJ/g	% Char[a]
EMI	0.0	18.8	NR	697	34	7.9
BDE	4.04	35.6	V0	704	20	26.3

[a] Microscale combustion calorimetry; values reported are the averages determines with a deviation of <5%.



Scheme 3. Potential Degradation Pathway for BDE Hardner in Epoxy Resin.

been prepared by treatment of desoxyanisoin with DOPO followed by acid-catalyzed ether cleavage to convert the methoxy groups to hydroxyls. This compound, 1-dopyl-1,2-(4-hydroxyphenyl)ethene (BDE), is an effective curing agent for DGEBA. The fully cured resin is thermally stable (onset of thermal decomposition at 417 °C) with a glass transition temperature, Tg, of 146 °C. This material contains 4% phosphorus and displays outstanding flammability characteristics – an LOI of 36, a total heat release of 20 kJ/g and a UL 94 V0 rating. This is reflective of a combination of both solid-phase (26% char formation) and gas-phase activity (DOPO decomposition).

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

CRediT authorship contribution statement

Bob A. Howell: Conceptualization, Methodology, Project administration, Supervision, Writing - original draft. **Gavan W. Lienhart:** Investigation. **Veronica J. Livingstone:** Validation. **Darpandeep Aulakh:** Validation.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.polymdegradstab.2020.109110.

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