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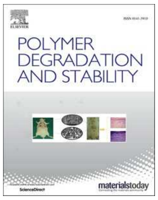

Synthesis of a phosphorus-based epoxy reactive flame retardant analog to diglycidyl ether of bisphenol A (DGEBA) and its behavior as a matrix in a carbon fiber composite

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ABSTRACT

This paper describes the synthesis of a phosphorus-based flame retardant that is a chemical analog of diglycidyl ether of bisphenol A (DGEBA), as well as its incorporation as a matrix into carbon fiber laminates. Carbon fiber composites, if used for structural applications in mass transport vehicles (aircraft, trains), will require some aspects of improved fire performance to be used safely in those applications. The first phase of work involved the development of two separate synthesis routes to produce the flame retardant monomer, referred to as Phosphorus-DGEBA or simply P-DGEBA. The second step was to determine the viability of the compound's polymerization behavior through various experimental mixing formulations and curing conditions with an aliphatic amine curing agent. Differential scanning calorimetry (DSC) was used to evaluate the curing behavior of P-DGEBA when mixed with DGEBA and an aliphatic amine curing agent and dynamic mechanical analysis (DMA) was used to observe the glass transition temperature (T_g) of the carbon fiber composites. Thermogravimetric analysis (TGA) was also used to investigate the thermal stability and thermal degradation behaviors of the P-DGEBA/DGEBA blends. The final step included the fabrication of composites and their flammability testing using a cone calorimeter. DMA testing for P-DGEBA measured a T_g that was 10 °C higher than a DGEBA based carbon fiber composite, and DSC studies found that the P-DGEBA / DGEBA blend polymerized well with the amine curing agent. The TGA, MCC, and cone calorimeter data yielded mixed results with TGA and MCC suggesting a more condensed phase / char formation flame retardant activity for P-DGEBA, while cone calorimeter suggested a more vapor phase flame retardant activity. Overall, the P-DGEBA shows some promise as a reactive FR for epoxy + carbon fiber composites, but more study is needed.

1. Introduction

Fiber-reinforced polymer matrix composites products are commonly used advanced materials and are found in virtually any commodity used in our everyday lives. Due to their superior mechanical properties, chemical resistance, and corrosion resistance, the use of polymeric composite materials continues to increase significantly, but their flammability behavior poses a major drawback preventing their wider use [1,2]. The combustion behavior of the polymer resin dominates the softening process, resulting in a loss of stiffness and strength in the composite material, which may result in structural failure particularly under compressive stress when the composite is in a fire event. As a result, the polymer matrix's resistance to fire is critical for the composite structure to preserve structural integrity during a fire and to prevent further flame spread in a fire event. Epoxy based thermosetting polymers are the most widespread matrix material used in various industries including aerospace, infrastructure, and transportation. In addition, the value of these composites has become even more emphasized by their applications in diverse areas of research, technology, and manufacturing [3]. The rising demand for these goods with a general understanding of their potential as fire hazards has rendered the ongoing polymer flammability problem a major challenge to our existing technologies [4,5]. The development of high thermal stability / low flammability epoxy resins has therefore become very important in academia and industry.

Commercial flame retardants do exist for epoxies but are limited when fiber reinforcement is required [6,7]. Therefore, successful flame

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retardants for epoxies must be compatible with epoxy manufacturing processes and should not filter out or migrate out during the manufacturing process. This means flame retardants which can react into the epoxy during manufacture are ideal, provided those flame retardants do not degrade other non-fire related properties, such as mechanical properties and thermal (glass transition temperature) properties. Many approaches have been applied to increase the flame retardancy of epoxy resin systems. Halogenated compounds have been commonly used as co-monomers or additives to produce flame retardant products, which act as flame poisoners in a fire situation. However, upon decomposition these flame retardants can also create corrosive smoke (due to formation of HCl and HBr which can be problematic in particular fire risk scenarios). Consequently, researchers need to find an effective alternative and environmental-friendly flame retardant for epoxy resins to protect the environment and human health.

Usually, the most efficient way to improve epoxy resin system flammability is by integrating a flame retardant compound into the epoxy matrix structure through covalent bonding (i.e., reactive flame retardant) so that the flame retardant cannot migrate out of the polymer over time. To this end, there have been several studies involving phosphorus-based compounds that can be inserted into either the epoxy monomer backbone or the curing agent. The majority of these new epoxy thermoset polymers displayed good flame retardancy at high phosphorus concentrations, but they required an excessive quantity of phosphorus to achieve the desired level of V-0 in UL94 testing and acceptable performance in LOI testing [8–17]. Furthermore, several of the aforementioned studies used elevated temperatures throughout the formulation process, making handling and production procedures more challenging. As a result, providing epoxy with self-extinguishing capabilities at low loadings of flame retardant materials and with ease of processing remains as a key challenge.

Epoxy resins are used extensively as a matrix for continuous fiber carbon composites. Only a few published research studies have examined the behavior of flame retarded carbon fiber composites with reactive phosphorus based FRs in cone calorimetry testing [11,18,19]. Their findings revealed a significant decrease in the peak heat release rate (PHRR) and total heat evolved (THE). However, these composites included less than one-third of combustible polymer matrix, which is typical for high fiber volume fraction composites used in aerospace.

The current study aims to examine the efficacy of a phosphorous based flame retardant epoxy monomer used at various concentrations in a common epoxy-amine resin blend. This monomer contains a phosphine oxide (P=O) functional group connected to two phenyl rings and a methyl group, but the phenyl rings include epoxide groups as well. This effectively creates a phosphorus flame retardant analog of diglycidyl ether of bisphenol A (DGEBA). Based upon a literature review, this particular reactive flame retardant has not been studied for its flame retardant effect in carbon-fiber reinforced composites. This study first examined the behavior of neat resin samples and determined a reasonable concentration that balances mechanical and thermal performance while minimizing the required loading of flame retardant. Following that, the results guided manufacturing of carbon fiber-reinforced composites with reasonably high fiber volume (0.5), and their flammability and mechanical characteristics were evaluated.

2. Experimental

2.1. Chemical synthesis and analysis

^{1}H and ^{13}C spectra were recorded at 300 MHz and 75 MHz respectively and referenced to the solvent ($CDCl_3$: 7.27 ppm and 77.0 ppm; DMSO-d_6: 2.49 ppm and 39.5 ppm). ^{31}P NMR spectra were obtained at 121 MHz and referenced to H_3PO_4 solution in DMSO-d_6 (0.0 ppm) or a $(CH_3O)_3P$ solution in $CDCl_3$ (141.0 ppm). The referencing for the ^{31}P NMR spectra was accomplished by measuring and calibrating the signal of the standard, followed by subsequent use of the Spectrum Reference (SR) feature of the NMR instrument, to standardize the rest of the spectra. Elemental analysis was provided by Atlantic Microlab, Norcross, GA. *Tris*(4-methoxyphenyl)phosphine was purchased from Arctom Chemicals. Oxone® monopersulfate compound was acquired from Sigma-Aldrich. The remaining commercial reactants/reagents were purchased from Thermo-Fisher Scientific, and were all analytical grade chemicals and solvents.

The generation of compound **4**, following ***Route A***, was accomplished using a previously reported protocol [20]. However, given the modifications of the procedures for preparation and isolation of compounds **3** and **4**, as well as the missing spectroscopic data in the original publication, we deemed it beneficial to describe both the details on synthesis and the spectroscopic data for those compounds. Methylphosphonyl dichloride [21] and *p*-bromophenyl allyl ether (**5**) [22] were synthesized, using available established procedures, without modification. Images of the NMR spectra for the substances reported in this paper are included in the Supplementary Information (Figs. S1–S4).

Di(*p*-methoxyphenyl)methylphosphine oxide (3). A mixture of tris(*p*-methoxyphenyl)methylphosphonium iodide **2** (26.40 g, 53.40 mmol), water (150 mL) and 40% *aq.* KOH (37 mL) was heated and stirred in a bath with temperature 130–140 °C, until the steam distillation of anisole ceased. The residual oil was extracted with benzene (4x), the combined benzene extracts were dried ($MgSO_4$), and the solution concentrated under reduced pressure, until the appearance of a white precipitate. Petroleum ether was added to the mixture, and the resultant copious white precipitation filtered under reduced pressure. This constituted most of the product, virtually pure. Additional amounts of product recovered *via* removal of the solvents from the mother liquor, under reduced pressure. White solid. Yield: 14.32 g (97%). ^{1}H NMR ($CDCl_3$) δ 1.92 (d, $J = 12.9$ Hz, 3H), 3.79 (s, 6H), 6.92 (dd, $J_1 = 8.5$ Hz, $J_2 = 2.0$ Hz, 4H), 7.59 (dd, dd, $J_1 = 11.4$ Hz, $J_2 = 8.6$ Hz, 4H); ^{13}C NMR ($CDCl_3$) δ 16.9 (d, $J = 74.4$ Hz), 55.2, 114.0 (d, $J = 12.9$ Hz), 125.5 (d, $J = 107.5$ Hz), 132.2 (d, $J = 11.2$ Hz), 162.1 (d, $J = 2.7$ Hz); ^{31}P NMR ($CDCl_3$) δ 29.7 (s, 1P).

Di(*p*-hydroxyphenyl)methylphosphine oxide (4). Di(*p*-methoxyphenyl) methylphosphine oxide **3** (12.00 g, 43.44 mmol) was dissolved in a mixture of 48% HBr (45 mL) and glacial AcOH (15 mL), and the resultant solution was stirred at 120 °C for 24 h. The mixture was cooled to ambient temperature, then slowly added to a vigorously stirred aqueous solution of Na_2CO_3 (roughly equivalent quantity, to neutralize HBr and AcOH, about 38 g of carbonate) at 0–5 °C (ice-water bath). White precipitate formed, somewhat sticky at first but gradually transitioning into a well-defined solid. The mixture was left slowly stirring for 24 h, the precipitate was filtered under reduced pressure through a medium-grade sintered glass filter, washed with small amount of cold water, and air dried. Off-white solid. Yield: 10.26 g (95%). ^{1}H NMR (DMSO-d_6) δ 1.86 (d, $J = 13.2$ Hz, 3H), 6.84 (dd, $J_1 = 8.6$ Hz, $J_2 = 2.2$ Hz, 4H), 7.50 (dd, $J_1 = 11.0$ Hz, $J_2 = 8.6$ Hz, 4H), 10.13 (s, 2H); ^{13}C NMR (DMSO-d_6) δ 16.6 (d, $J = 73.6$ Hz), 115.4 (d, $J = 12.6$ Hz), 123.7 (d, $J = 106.7$ Hz), 132.1 (d, $J = 11.1$ Hz), 160.1 (d, $J = 2.7$ Hz); ^{31}P NMR (DMSO-d_6) δ 28.1 (s, 1P).

Di(*p*-allyloxyphenyl)methylphosphine oxide (6) [23]. In a flame-dried flask, equipped with an addition funnel, were placed magnesium turnings (2.17 g, 89.70 mmol) and anhydrous THF (70 mL), while *p*-bromophenyl allyl ether **5** (19.11 g, 89.70 mmol, 13.0 mL), dissolved in anhydrous THF (60 mL), was introduced into the addition funnel. 1,2-Dibromoethane (about 0.05 mL) was added to the flask and the mixture stirred upon heating, to initiate the reaction. Then some quantity of the solution from the addition funnel was added, to start the formation of the Grignard reagent. The process was exothermic, so the dropwise addition of the rest of the solution in the addition funnel was adjusted, so as to ensure the reaction occurring at a moderate rate. Stirring continued for 1 h, at which point all of the Mg had reacted. In the meantime, the addition funnel was charged with a solution of methylphosphonyl dichloride (5.96 g, 44.85 mmol, 4.10 mL) in anhydrous THF (25 mL) (*Note: Methylphosphonyl dichloride is a low melting*

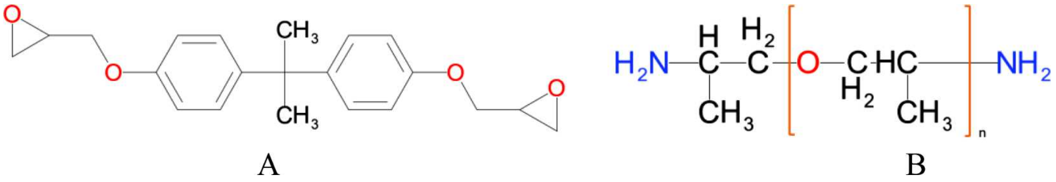


Fig. 1. Baseline resin system monomers: (A) DGEBA (EPON 825), and (B) Polyoxypropylene diamine (EPIKURE 3274, which also includes nonylphenol).

solid, so one has to heat it slightly, in order for it to liquefy and measure the needed amount volumetrically). The reaction flask was immersed into an ice – water bath, then the solution in the addition funnel was added dropwise, over ~20 min period. Stirring continued at ambient temperature for 1 h, followed by 3 h at 80 °C, then overnight at ambient temperature. The reaction mixture was poured into *aq.* NH_4Cl, the organic layer separated, and the aqueous layer extracted twice with ether. The combined organic layers were washed with brine, dried ($MgSO_4$), and the solvents removed under reduced pressure. The resultant oily residue slowly solidified. Hexane/toluene mixture (10:1) was added to the flask, the contents heated to reflux, cooled to ambient temperature, then cooled further with a dry ice-acetone bath, upon vigorous stirring. The oily material solidified, the solid was filtered under reduced pressure, washed with hexane and dried. Off-white powder. Yield: 12.09 g (82%). ^{1}H NMR ($CDCl_3$) δ 1.94 (d, $J = 13.2$ Hz, 3H), 4.55 (d, $J = 5.3$ Hz, 4H), 5.29 (dd, $J_1 = 10.5$ Hz, $J_2 = 0.7$ Hz, 2H), 5.40 (dd, $J_1 = 17.3$ Hz, $J_2 = 1.3$ Hz, 2H), 5.96–6.09 (m, 2H), 6.97 (dd, $J_1 = 8.6$ Hz, $J_2 = 2.1$ Hz, 4H), 7.61 (dd, $J_1 = 11.4$ Hz, $J_2 = 8.4$ Hz, 4H); ^{13}C NMR ($CDCl_3$) δ 17.0 (d, $J = 74.4$ Hz), 68.8, 114.8 (d, $J = 12.6$ Hz), 118.1, 125.7 (d, $J = 107.5$ Hz), 132.3 (d, $J = 11.1$ Hz), 132.6, 161.2 (d, $J = 2.8$ Hz); ^{31}P NMR ($CDCl_3$) δ 29.6 (s, 1P).

Methyl*bis*(4-(oxiran-2-ylmethoxy)phenyl)phosphine oxide (P-DGEBA, 1). ***Route A:*** Di(*p*-hydroxyphenyl)methylphosphine oxide **4** (2.00 g, 8.08 mmol), epichlorohydrin (20.20 g, 218.16 mmol, 17.0 mL) and tetramethylammonium bromide (TMAB, 20 mg, 0.0808 mmol) were mixed in a flame-dried flask, purged with nitrogen, and the resultant mixture was stirred at 150 °C for 3 h, under nitrogen. The temperature was then reduced to 60 °C and 50% *aq.* NaOH (0.32 g NaOH in 0.32 mL of water) was added portion wise, with stirring. The mixture was stirred for additional 12 h, at ambient temperature. Poured into methylene chloride, the organic layer was separated, washed three times with water, followed by brine, dried (Na_2SO_4), and the solvent/volatiles removed under reduced pressure. The oily residue was separated on a silica gel column (acetone: methylene chloride = 2: 1). White solid. Yield: 2.10 g (72%). Mp 72–74 °C. ^{1}H NMR ($CDCl_3$) δ 1.96 (d, $J = 13.2$ Hz, 3H), 2.77 (dd, $J_1 = 4.8$ Hz, $J_2 = 2.6$ Hz, 2H), 2.92 (t, $J = 4.5$ Hz, 2H), 3.34–3.38 (m, 2H), 3.97 (dd, $J_1 = 11.1$ Hz, $J_2 = 5.8$ Hz, 2H), 4.29 (dd, $J_1 = 11.1$ Hz, $J_2 = 2.9$ Hz, 2H), 6.99 (dd, $J_1 = 8.8$ Hz, $J_2 = 2.1$ Hz, 4H), 7.62 (dd, $J_1 = 11.3$ Hz, $J_2 = 8.7$ Hz, 4H); ^{13}C NMR ($CDCl_3$) δ 16.8 (d, $J = 74.5$ Hz), 44.4, 49.8, 68.6, 114.6 (d, $J = 12.7$ Hz), 126.0 (d, $J = 107.1$ Hz), 132.2 (d, $J = 11.1$ Hz), 160.9 (d, $J = 2.8$ Hz); ^{31}P NMR ($CDCl_3$) δ 29.6 (s, 1P); Anal. Calcd. for $C_{19}H_{21}O_5P$: C, 63.33; H, 5.87. Found: C, 63.19; H, 6.04.

Route B: Di(*p*-allyloxyphenyl)methylphosphine oxide **6** (6.60 g, 20.13 mmol) was introduced into a three-neck round-bottom flask, equipped with a mechanical stirrer and a solid addition funnel. Actone (80 mL) was added to the flask, followed by solid $NaHCO_3$ (11.50 g, 136.90 mmol). The mixture was placed into an ice-water bath, followed by addition of Oxone® monopersulfate compound (24.0 g, 78.08 mmol, Sigma-Aldrich), dissolved in water (80 mL), over a period of 15 min. The resultant mixture was stirred vigorously for 18 h at ambient temperature. A second batch of $NaHCO_3$ (11.50 g) and Oxone (24.00 g) was added, followed by stirring for 6 h. A third batch of $NaHCO_3$ (11.50 g) and Oxone (24.00 g) was added, and the stirring continued for additional 18 h, at ambient temperature. Sufficient amount of water was aadded, to ensure the dissolution of the solids, then the mixture was extracted twice with ethyl acetate. The combined organic layers were washed with water, followed by brine, dried (Na_2SO_4), and the solvents removed under reduced pressure. The remaining clear colorless oily residue solidified. Yield: 6.09 g (84%). NMR indicated a virtually pure target compound **1**. Spectroscopic properties were a complete match of those for the compound produced following ***Route A***.

2.2. *Epoxy resin system formulation*

The baseline epoxy resin system used in this project was the bisphenol A epichlorohydrin epoxy resin (EPON 825), with a low viscosity aliphatic diamine as a curing agent (Hexion EPIKURE 3274); (see Fig. 1) for chemical structures. The theoretical epoxide equivalent weight (EEW) of EPON 825 was 170 g/equiv., while the amine hydrogen equivalent weight (AHEW) of Epikure 3274 was 76 g/equiv. The purpose of choosing EPON 825 was because it is the closest chemical analog to P-DGEBA and it is high purity (i.e. no isomers). EPIKURE 3274 was chosen because it is able to cure at or near room temperature with DGEBA. This resin system is suitable for the vacuum assisted resin transfer molding (VARTM) process. VARTM is used to make large composite structures in infrastructure, transportation, and marine applications, all of which flame retardancy is a key issue.

A total of approximately 25 g of P-DGEBA was synthesized in this study, utilizing both methods *A* and *B*. Large scale runs following *route A* generally produced a material that was a colorless oil, requiring more strenuous chromatography separation in order to solidify. The material produced following *route B* was a solid, with slight variations in color (see Fig. 2). These differences were attributed to minor impurities, admixed into the product in the case of *route A*, while *route B* produced material of higher purity, generally not requiring any further

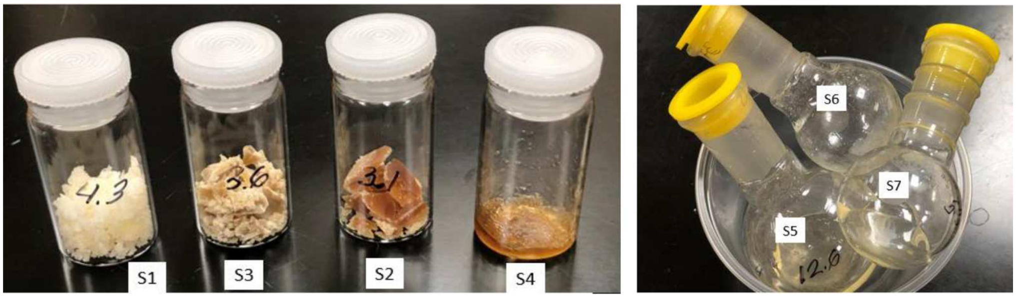


Fig. 2. Collection of P-DGEBA samples synthesized in this study. S1–S4 were synthesized by *route B* while S5–S7 were synthesized by *route A*.

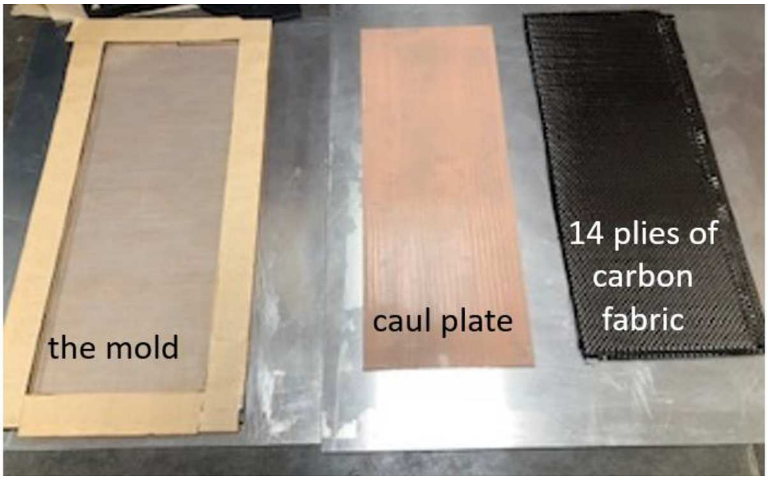


Fig. 3. Panel mold details.

purification. Because the amount of material was insufficient for scale up and making plaques for cone calorimeter testing, it was decided to blend P-DGEBA with EPON 825 which has a similar structure and functionality. Since they have similar molecular weights (within ~5%), the theoretical EEW values were also expected to be similar. The actual EEW values were not measured in this study. Therefore, the usual stoichiometric formulation of EPON 825 (or EPON 825 + P-DGEBA) at 69 wt.% and EPIKURE 3274 at 31 wt.% was used as a basis for all mixtures. For early testing requiring small samples, P-DGEBA was diluted with EPON 825 in the following proportions: 75/25, 50/50, 25/75 wt/wt P-DGEBA/EPON 825. For composite fabrication, only the 50/50 blend was used due to the limited quantity of material. All P-DGEBA samples were dried in a convection oven at 100 °C for 1 h prior to use.

As mentioned, the P-DGEBA samples were produced in different batches and with two different synthesis procedures, which resulted in several samples of different color and rheology (some were viscous liquids while others were solid). Before blending them in one container, thermogravimetric analysis (TGA) was used to investigate the moisture content and residual solvent in each sample, and the viscosity of each was measured with a parallel plate rheometer (See TGA results are included in the Supplementary Information Figs. S5–S7). After all initial testing of neat resin was complete, a total of 14.37 g of P-DGEBA from *route A* and 8.52 g from *route B* was available for composite fabrication, as described in the next section. There was not enough material to make neat resin plaques for cone calorimeter testing.

To provide enough material for composite fabrication, P-DGEBA was blended with EPON 825 in a 50/50 weight ratio so as to maximize the supply of P-DGEBA. First, the three *route A* liquid P-DGEBA samples were blended with EPON 825 in one plastic mixing cup (Flacktek, max 50 g cup). This was mixed for 5 min at 2500 RPM in a FlackTek SpeedMixer model DAC 330-100 SE (Flacktek SpeedMixer, Landrum SC, USA). Next, the same technique was followed for the *route B* solid P-DGEBA samples, except that heating to 100 °C was required to liquefy them and remove as much material as possible from each container. There was a significant difference in hue between the two mixtures, reflecting the fact that the two samples were extracted using different techniques and solvents. In the final step, the Route A and Route B blends were uniformly mixed for five minutes at 2500 RPM in the FlackTek SpeedMixer at room temperature, resulting a yellow-colored liquid blend. The overall weight of the combined 50/50 P-DGEBA/EPON 825 blend was about 46 g.

2.3. Composite fabrication

Due to the small quantity of P-DGEBA avalible, selecting a composite manufacturing technique was challenging because most processes involve some wasted resin such as vacuum infusion. Several techniques were investigated that could be applied to small scale samples, using the baseline resin system (EPON 825 / Epikure 3274) as a model resin system to develop a suitable technique that led to no waste resin. Various methods were tried, all involving a wet layup process followed by compaction with a press, vacuum bag, or autoclave. In the end the only method that worked was the autoclave, while the other two methods were plagued with resin leakage issues. The wet layup and autoclave cure process is described next.

The reinforcement selected was a plain weave carbon fabric made from 3 K tows of standard modulus carbon fibers (Freeman Manufacturing and Supply Company, cat. # 404005, style 94901, 193 g/m^2). The panel dimensions were based on several criteria: (i) 3 mm thickness was desired for cone calorimeter testing, (ii) width was set at 11.4 cm (4.5 in.) in order to provide a sufficiently wide sample for cone calorimeter testing, and (iii) length was maximized to consume all the P-DGEBA assuming a fiber volume fraction (V_f) of 0.50. The strategy was to minimize waste by making one large plaque and cutting out 3 square samples for cone calorimeter testing. The final panel dimensions were 30.5 cm x 11.5 cm x 0.3 cm (12 in. x 4.5 in. x 0.12 in.), which allowed three square samples to be cut out for cone calorimeter testing, as well as a flexure coupon for DMA testing. After edge trimming, each square sample was 8.9 cm x 8.9 cm. x 0.3 cm (3.5 in. x 3.5 in. x 0.12 in.). The weight of mixed resin required for each big panel was 63.1 g (assuming a resin density of 1.2 g/cm^3). This equated to 43.54 g of epoxy, or 21.77 g of P-DGEBA since the 50/50 P-DGEBA/EPON 825 mix ratio was selected for composite fabrication. This consumed 95% of the available P-DGEBA, while the remaining 5% was accounted for as hang-up on the walls of the various sample containers and mixing cups involved throughout the process. This low level of loss was acceptable and further emphasizes the importance of the manufacturing method when considering flame retardant use and minimization of chemical/hazardous waste in composite manufacture.

A mold was fabricated by adhering a double thick layer of vacuum bag sealant (Tacky Tape SM5127) on an aluminum plate to frame an area of 30.5 cm x 11.5 cm, see Fig. 3. A layer of nonporous release ply (Release Ease 234 TFNP, Airtech International) was placed on the plate surface within the mold. Fourteen layers of carbon fabric (also 30.5 cm x 11.5 cm) were cut from the fabric bolt and set aside. Thus, the vacuum bag sealant was sized to become a resin dam to prevent resin bleed, as is common in autoclave molding. A caul plate was fabricated from a previously made carbon fiber laminate (~2 mm thick) which was cut to 30.5 cm x 11.5 cm and covered with a polymeric non-stick film (see Fig. 3, middle).

The resin system was prepared by adding the resin system components to a FlackTek max 60 g cup as follows: 43.54 g of P-DGEBA/EPON

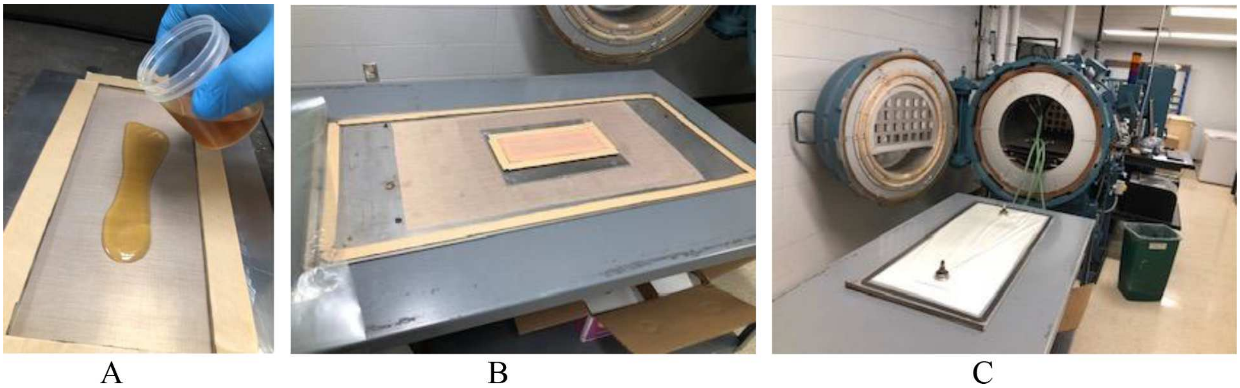


Fig. 4. (A) Pouring resin into the mold, (B) Mold assembly on autoclave base plate, (C) Vacuum bag assembly prior to curing.

826 50/50 blend, and 19.56 g EPIKURE 3274. The resin system for control panels was comprised of 43.54 g EPON 825 and 19.56 g EPIKURE 3274. The resin components were uniformly mixed at ambient temperature for 5 min at 2500 RPM in a FlackTek SpeedMixer. The mixture was then degassed at ambient temperature in a vacuum pot for 10 min.

Panel fabrication involved pouring the resin onto the bottom of the mold (see Fig. 4A), laying the fourteen layers of carbon fabric into the mold, and placing the caul plate on top. The mold assembly was placed on a larger steel base plate (Fig. 4B) and covered with a non-porous Teflon sheet to help prevent any resin migration if any escaped from the panel and sealant dam. Most of the baseplate was covered with a cotton breather ply (Airweave N10, Airtech International Inc.), and the entire plate was covered and sealed with a nylon vacuum bag (Wrightlon WL47400, Airtech International Inc.). The bag contained one port that led to a vacuum pump, and one port that led to a vacuum sensor (Fig. 4C). After a vacuum leak check, the plate and vacuum bag assembly was placed into the autoclave (Econoclave Model EC-2×4200P800F-2S2PT, ASC Process Systems Inc.).

The cure cycle was ambient to 71 °C (160 °F) at a rate of 5.6 °C/min (10 °F/min). The autoclave was pressurized with nitrogen to 309 kPa (45 psig) during the temperature ramp. The bag was vented to atmospheric pressure once 49 °C (120 °F) was reached. When the temperature reached 71 °C (160 °F) this temperature was held for 90 min. Next, the inside of the autoclave was cooled to room temperature at a target rate of 5.6 °C/min (10 °F/min). The pressure was released from autoclave when temperature dropped below 49 °C (120 °F). The final step was to post cure each panel free-standing in a convection oven at 100 °C (212 °F) for 1 h. A total of three control panels (no P-DGEBA) were produced to prove-out the process and verify repeatability. One panel containing P-DGEBA was then fabricated using the established procedures. Final coupons for cone calorimeter testing were cut out using a water-cooled diamond blade wet saw.

2.4. Resin and composite characterization

2.4.1. Differential scanning calorimetry (DSC)

The curing and decomposition behavior of P-DGEBA was investigated with a model Q2000 DSC unit (TA Instruments Inc., New Castle, DE, USA). DSC analysis was run on approximately 5 mg samples heated from 40 to 300 °C under a nitrogen flow of 50 mL/min and a heating rate of 10 °C/min to evaluate basic cure and decomposition behavior. Each sample was reheated from 40 to 150 °C at 10 °C/min to measure T_g. In addition, some freshly mixed resin was first cured in an oven at 170 °C for 2 h, and then tested in DSC for T_g.

Formulations with the following ratios of P-DGEBA to EPON 825 were tested: 0/100 (control), 25/75, 50/50, 75/25. Each of these blends was mixed with EPIKURE 3274 at a weight ratio of 69/31 epoxy blend/curing agent. All samples were tested in DSC immediately after mixing. No composite samples were tested with DSC.

2.4.2. Thermogravimetric analysis (TGA)

The thermal degradation behavior of fresh and cured samples was evaluated with a Q500 TGA unit (TA Instrument Inc.). All samples (5 mg) were placed in open platinum pans and then heated from 30 to 600 °C at a rate of 10 °C/min in nitrogen using an evolved gas analysis (EGA) furnace at a flow rate of 90 mL/min with a flow rate of 10 mL/min to the thermobalance. A sample of pure P-DGEBA from each of the seven synthesized batches was tested first to investigate moisture content or any residual solvent. Samples of 3-component formulations (P-DGEBA / EPON 825 / EPIKURE 3274) with various ratios of P-DGEBA to EPON 825 were also tested to evaluate thermal decomposition behavior and char yield at 600 °C under the same conditions. No composite samples were tested with TGA.

2.4.3. Micro combustion calorimetry (MCC) testing

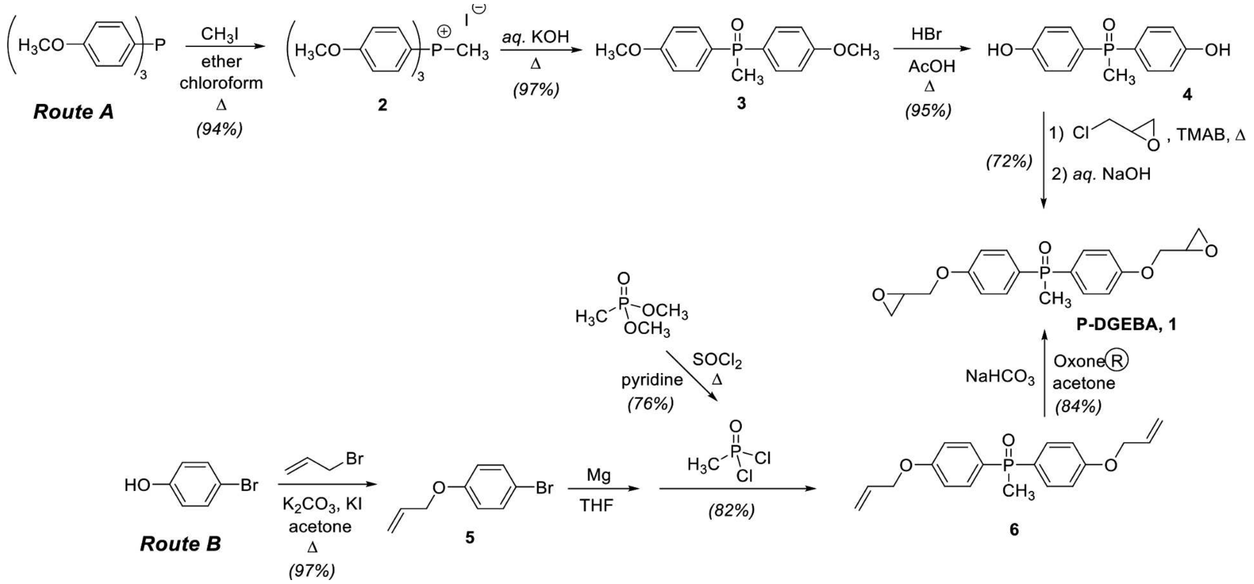
MCC (ASTM D7309) was utilized to conduct a first heat release reduction screening. MCC has been found to be an effective screening method for rapidly determining the flammability of materials when just a small quantity of material is available. Even though MCC has significant limitations in terms of what it can measure, it has remained a valuable tool for material development [24–28]. Due to the limited availability of P-DGEBA, the MCC test was the best tool for evaluating the effectiveness of various P-DGEBA/EPON 825 combinations and determining which blend fraction would be optimum for scaling up to create cone calorimeter testing plaques. MCC testing was performed on resin samples using ASTM D7309-21b (Method A) settings using a Deatak MCC-1 unit (McHenry, IL, USA). Samples were taken from the material that had been mixed for DSC testing. Each sample was post-cured in its aluminum boat in a convection oven at 100 °C for 1 h. Each formulation was tested three times, and a polystyrene control was provided for comparison. The final chars were weighed using a microbalance.

2.4.4. Dynamic mechanical analysis (DMA)

DMA was used to characterize cured composite samples, namely the control panel (no P-DGEBA) and the panel containing P-DGEBA / EPON 825 in 50/50 ratio. Specimen size was 6.35 cm x 1.27 cm x 0.3 cm (2.5 in x 0.5 in x 0.12 in). DMA testing was performed in 3-point bend mode with a 50 mm span length, a preload force of 0.1 N, 20 μm strain amplitude, and a frequency of 1 Hz. The heating cycle was 20–150 °C, at a rate of 3 °C/min. The glass transition temperatures (T_g) were determined at the peak of the tan (δ) curve.

2.4.5. Fiber volume fraction (V_f) estimation

To verfiy the fiber volume fraction (V_f) of the cured panels, two method were used. The first method was based on the density of each panel, where the rule of mixtures leads to the following equation:



Scheme 1. Synthesis of Phosphine Oxide Bisphenol A Epoxy (P-DGEBA).

$$V_f = \frac{\rho_c - \rho_R}{\rho_f - \rho_R} \tag{1}$$

where ρ_c is the density of composite, ρ_R is the density of the cured resin, and ρ_f is the density of fiber (1.78 g/cm^3). The density of the composite was measured with a water displacement technique (ASTM D792) using a Mettler Toledo balance and density fixture. Three small samples were tested from each of the four composite panels (3 control panels, 1 panel containing P-DGEBA). The resin density was tested from small pieces of neat resin extracted from the sides of the panels and mold walls.

The second method was based on the cured ply thickness (CPT) of each panel using following equation (assumes no voids):

$$V_f = \frac{FAW}{\rho_f \ x \ CPT} \tag{2}$$

where FAW is the areal weight of the fabric (0.0193 g/cm^2), ρ_f is the density of the fiber (1.78 g/cm^3), and CPT is the cured ply thickness (cm) of the panel. CPT was determined by measuring the thickness of three cone calorimeter coupons produced in each autoclave run using a caliper and calculating the average thickness of the three panels.

2.4.6. Optical microscopy

One sample of each panel was potted in epoxy and polished with a Buehler Automet/Ecomet 250 rotary grinding/polishing unit. A Zeiss AX10 microscope was used to analyze the cross section of each sample for porosity and general quality.

2.4.7. Cone calorimeter equipment and parameters

The heat and smoke release characteristics of the 8.9 cm x 8.9 cm (3.5 in x 3.5 in) composite plaques were evaluated using Deatak CC-2 Cone Calorimeter (Deatak, McHenry, IL USA). The usual 100 mm x 100 mm (4 in. x 4 in.) coupon size was not used due to the reasons explained above (scarcity of P-DGEBA). The area of 0.00792 m^2 was input into the parameters section for calculations. The composite samples were made with woven carbon fiber using EPON 825 / EPIKURE 3274 as a baseline, and (50%EPON/50%P-DGEBA) / EPIKURE 3274 as the flame retardant matrix. Each material was examined in triplicate, using a 3 mm sample thickness. Cone calorimeter experiments were conducted using the standardized cone calorimeter procedure (ASTM E-1354-21) at one heat flux (50 kW/m^2) and a 24 L/s exhaust flow. The ASTM E-1354 standard requires that samples be wrapped in aluminum foil on one side, and that was used during testing. A frame or grid was not needed for these samples.

3. Results and discussion

3.1. Chemical synthesis

(A) *Synthesis of the P-containing analog of diglycidyl ether of bisphenol A* ***(P-DGEBA, 1)***. The target compound **P-DGEBA** was prepared utilizing two different synthetic protocols, routes ***A*** and ***B*** correspondingly (Scheme 1. Synthesis of P-DGEBA).

Route A is largely based on a previously reported protocol, at least the part concluding with the generation of di(*p*-hydroxyphenyl)methylphosphine oxide **4** [20]. It starts with *tris*(4-methoxyphenyl)phosphine, which is reacted with methyl iodide, to form the phosphonium salt **2**. The latter is converted, upon reaction with hot aqueous KOH to di(*p*-methoxyphenyl)methylphosphine oxide **3**, which is then cleaved with hydrobromic acid to di(p-hydroxyphenyl)methylphosphine oxide **4**. These reactions were conducted with some modifications of the original protocol, and all occurred with high, reproducible yields. The final step, the generation of P-DGEBA from compound **4**, exploited an adaptation of established procedures [29,30]. Large excess of epichlorohydrin was used, requiring the removal of residual quantities upon workup.

The preparation, following ***Route B***, starts with the generation of *p*-allyloxybromobenzene (**5**), *via* reaction of *p*-bromophenol with allyl bromide in basic conditions [22]. Compound **5** is then converted into the corresponding Grignard reagent, and the latter reacted with methylphosphonyl dichloride [21], to produce di(*p*-allyloxyphenyl)methylphosphine oxide **6** [23]. Earlier attempts to use dimethyl methylphosphonate, instead of methylphosphonyl dichloride, were not successful. Finally, epoxidation of the phosphine oxide **6**, following a previously reported protocol using Oxone®, leads to generation of compound **1** (**P-DGEBA**) [31]. Yield of compound **1** was optimized by the use of large excess of Oxone, and introduction of the latter in several portions, with relatively long reaction times in-between.

Overall, ***Route B*** is advantageous, as it utilizes inexpensive starting materials and produces raw samples of **P-DGEBA** which require no further purification. In contrast, the crude product, produced following ***Route A*** does require chromatographic separation.

3.2. Epoxy-amine resin formulation

DSC traces for the baseline resin system and P-DGEBA containing

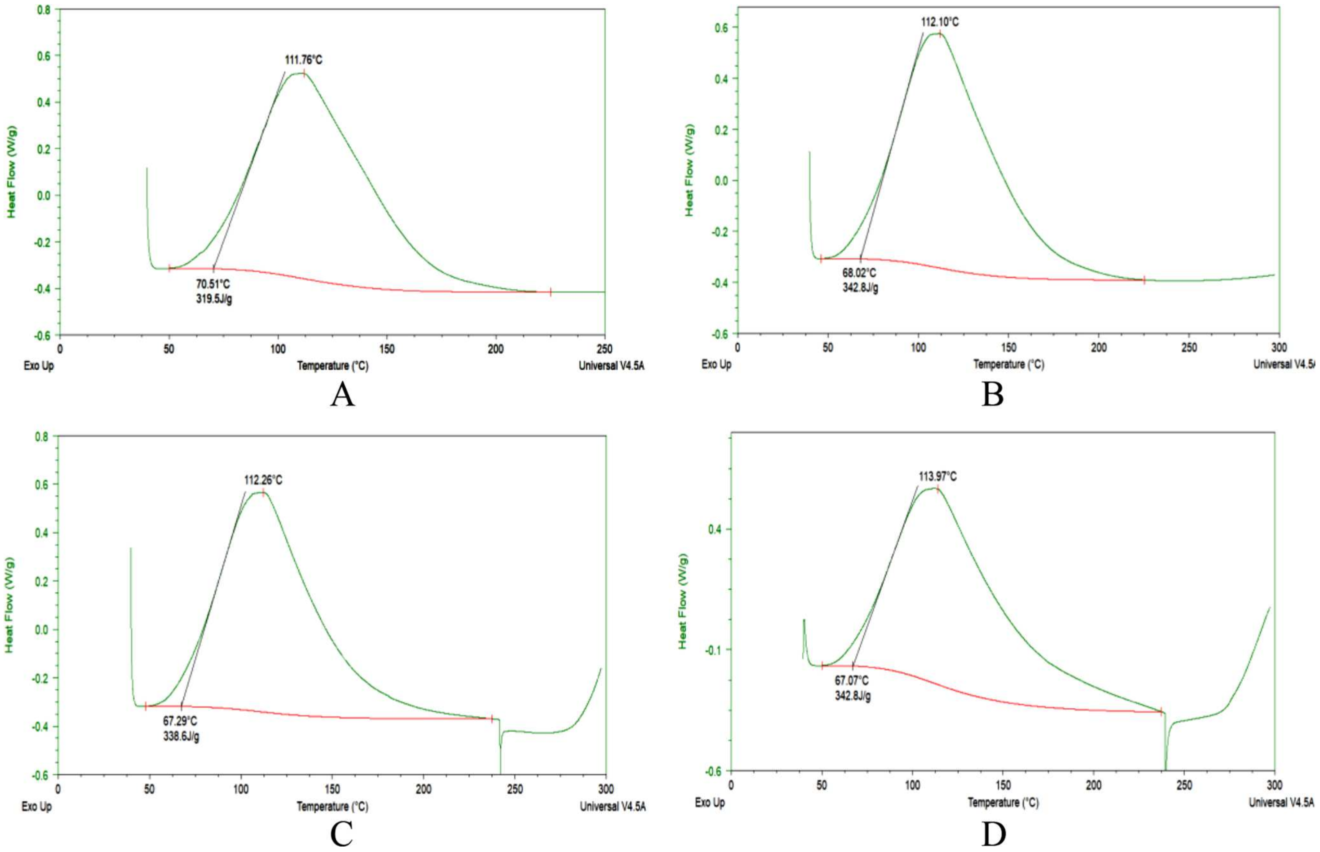


Fig. 5. DSC results for: (a) Baseline resin, (b) 75 EPON 825 / 25 P-DGEBA, (c) 50 EPON 825/50 P-DGEBA, and (d) 25 EPON 825 / 75 P-DGEBA. In all cases, the combined epoxy resin components are present at 69 wt% and EPIKURE 3274 at 31 wt%.

Table 1
DSC results for P-DGEBA / EPON 825 blends (each mixed with 31 wt% EPIKURE 3274). α is degree of cure.

P-DGEBA/ DGEBA formulation (wt%/wt%)	Onset of cure T (°C)	Heat of reaction (J/g)	Peak T (°C)	T_g upon DSC reheat (°C)	T_g after oven cure (°C)	α after oven cure (%)
Baseline (0 P-DGEBA)	70.5	319.5	111.8	56.8	68.5	100
75 EPON/25 P-DGEBA	68.0	342.8	112.1	65.8	69.4	96
50 EPON/50 P-DGEBA	67.3	338.6	112.3	68.0	72.9	95
25 EPON/75 P-DGEBA	67.1	342.8	114.0	55.3	76.1	98

blends are given below in Fig. 5. In each formulation the cure reaction began around 50 °C and continued to over 200 °C, although the peak was around 112 °C. The heat of reaction, approximately 320 J/g, was within the typical range for many epoxy resins (300–600 J/g), and the curves were very similar. The samples with the highest levels of P-DGEBA (Fig. 5C, D) both exhibited a sharp endotherm at 240 °C. It is suspected that the production and escape of vapor from the decomposition of P-DGEBA contributed to this.

The DSC results are summarized in Table 1. As seen, the heats of reaction of P-DGEBA containing samples were slightly (~6%) higher compared to the baseline sample. It is assumed the presence of Phosphorus (as phosphine oxide) in the DGEBA does not affect the heat of reaction since it does not participate in the reaction of epoxy and amine. Although it could possibly catalyze the reaction, this would speed up the reaction but not affect the total heat of reaction. The molecular weight of P-DGEBA is about 6% higher than EPON 825. Therefore, because the weight ratios were kept the same for all formulations (69 epoxy / 31 curing agent), the stoichiometry slightly deviates from 1:1, leading to a slight deficit in epoxy as the level of P-DGEBA increases (for example 1:1 for baseline sample, 1:1.03 for the 50% sample, and 1:1.06 for a sample with 100% P-DGEBA). It is generally known for epoxy-amine resin systems that some excess of amine curing agent can increase the extent of reaction because some secondary amine groups never react. This may explain the higher heats of reaction for P-epoxy formulations.

The glass transition temperatures of P-DGEBA samples were slightly higher than the baseline sample. This may also be due to the reasons given above (i.e. uncertainty in EEW – there may have been excess amine which leads to more complete conversion of epoxy). The oven-cured material consistently produced higher T_g than that obtained in the DSC reheat cycle. This may be attributed to thermal decomposition in the first cycle (i.e. max temp of 300 °C compared to 170 °C in the oven).

The thermal decomposition behavior of the oven-cured resin samples was observed from TGA thermograms as shown in Fig. 6, and the numerical results are summarized in Table 2. TGA results show that P-DGEBA epoxy resins thermally decomposed in the relatively low-temperature region (300–330 °C), with the onset weight loss temperaure steadily declining as the proportion of P-DGEBA increased. This was attributed to the decomposition of the P-DGEBA molecules which would provide flame poisoning benefits (or potential char formation) in a fire scenario. However, at the region of temperatures higher than 400 °C, the decomposition rates of the P-DGEBA resins were observed as being slower than the decomposition rates of the baseline resin. In addition, the char yields of the samples increased steadily as the proportion of P-DGEBA increased. Greater char formation may help restrict the generation of combustible gases, reduce the exothermicity of the

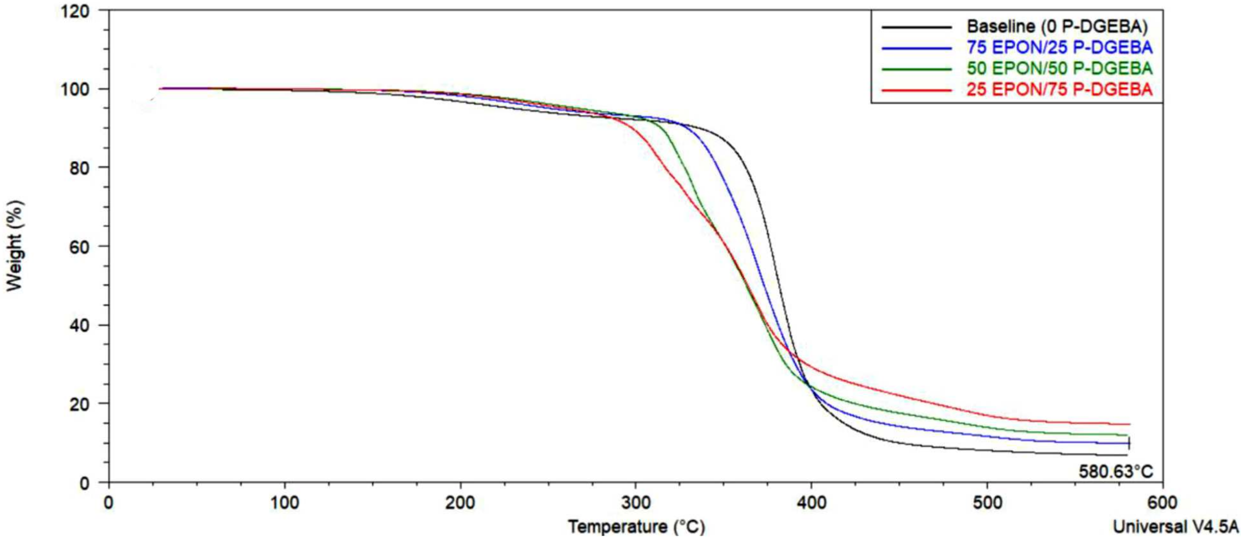


Fig. 6. TGA results for oven-cured resin samples. In all cases, the combined epoxy resin components are present at 69 wt% and EPIKURE 3274 at 31 wt%.

Table 2
TGA results taken from Fig. 6 for oven cured resin samples (each mixed with 31 wt% EPIKURE 3274).

P-DGEBA/DGEBA formulation (wt %/wt%)	Onset of decomposition T (°C)	Char yield (wt %)
Baseline (0 P-DGEBA)	358.1	6.8
75 EPON/25 P-DGEBA	335.0	9.9
50 EPON/50 P-DGEBA	306.6	12.0
25 EPON/75 P-DGEBA	306.4	14.8

pyrolysis process, and reduce the thermal conductivity of burning materials. The P-DGEBA epoxy resins produced more char than the baseline epoxy resins, indicating that the phosphorus epoxy resins have promising flame retardant properties, and are showing some effects of a condensed phase (char formation) mode of action/mechanism of flame retardancy. The TGA data suggests that there are some changes to thermal decomposition chemistry for the epoxies containing increasing levels of P-DGEBA. This is suggested by the earlier onset of thermal decomposition, and with further study of the MCC data discussed in Section 3.4 of this manuscript. Based upon known chemical bond strengths, it can be hypothesized that the C-P bonds (namely the phenyl carbon bonding to the phosphorus) are breaking first, thus forming phenyl radicals and P=O methyl/phenyl radicals that undergo additional decomposition along with some crosslinking to yield higher levels of char. Further study would be needed to verify this hypothesis.

3.3. Composite fabrication and initial characterization

Dilution of P-DGEBA by 50% wt. with EPON 825 was taken as the optimum formulation because of the reasonable balance of curing behavior, T_g, and thermal stability as observed in DSC and TGA results. Dilution of P-DGEBA with EPON 825 was deemed a suitable way to proceed since the flame retardant's essential properties were retained in the blended systems (higher char yield, change in onset decomposition). Additionally, considering the limited quantity of P-DGEBA available, dilution with EPON 825 by 50 wt% lowered the total amount of pure P-DGEBA necessary for cone calorimeter testing by two (compared to using 100% P-DGEBA) while maintaining the blend's flammability properties. Use of the blended resin system as a *composite matrix* also reduced the required amount of P-DGEBA, especially at a matrix volume fraction of 0.5. Overall, this study made very efficient use of a limited amount of the synthesized monomer. A photo of the composite panels after trimming them into cone calorimeter coupons is given in Fig. 7. It was simple to release the samples from the mold as they had smooth surfaces on both sides and no visible defects or dry spots. Three trials were conducted with the baseline resin system to boost confidence and guarantee that the process was repeatable before attempting the panels containing P-DGEBA. The panels containing P-DGEBA did not appear any different visually than the control panels. Optical microscopy confirmed no noticeable voids, defects, or questionable areas in all samples, see Fig. 8.

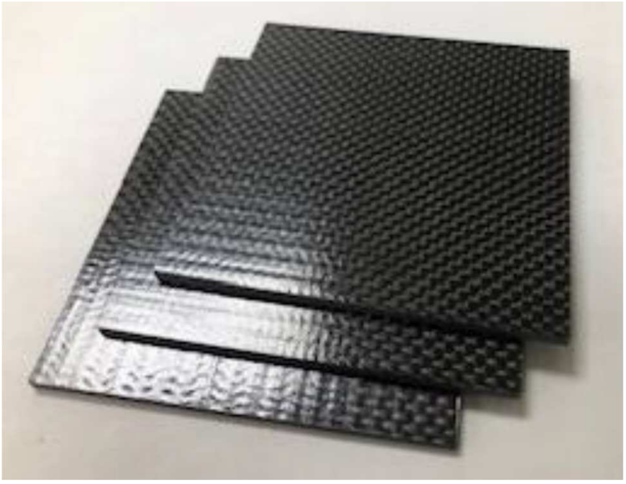


Fig. 7. Cured composite panels trimmed to size (8.9 cm x 8.9 cm) for cone calorimeter testing. Three coupons like these were obtained in each autoclave molding run.

The density results of the composite panels obtained from the water displacement method are summarized in Table 3. Also given are the density values of neat resin samples obtained as small pieces of resin flash taken from the sides of the panels and/or mold walls. The average composite density was approximately 1.463 g/cm^3 with a standard deviation of 0.017 g/cm^3 (1.1% coefficient of variation across all 9 samples measured). The panel containing P-DGEBA was significantly (1.9%) higher at a density of 1.491 g/cm^3. This difference was attributed to the higher density of the P-DGEBA-containing resin, which was 1.173 g/cm^3 compared to an average of 1.137 g/cm^3 for the baseline resin system (both in the cured state). The P-DGEBA-containing resin density was therefore 3.2% higher than the baseline resin. Using the rule of mixtures

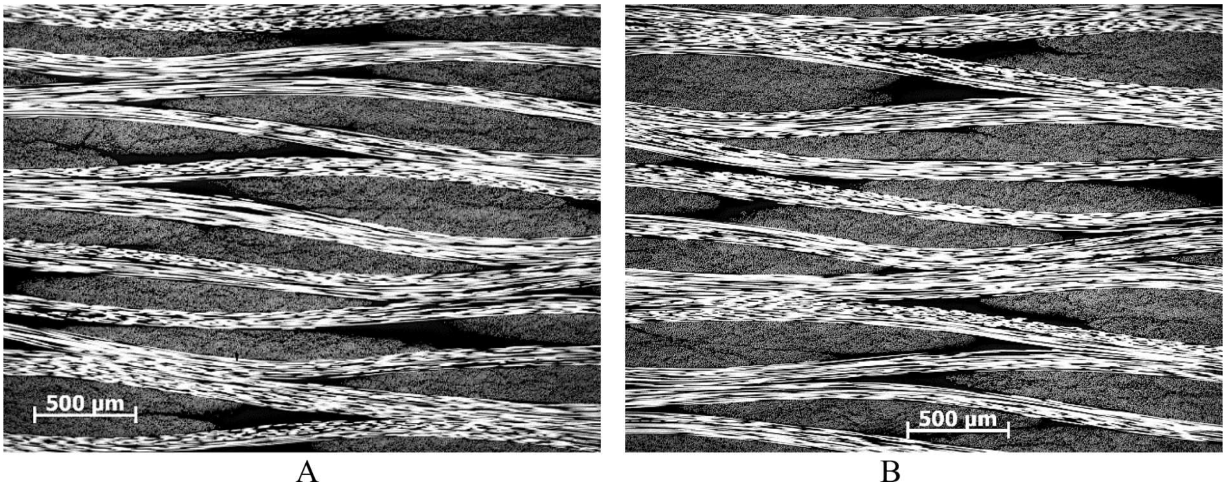


Fig. 8. Optical microscopy results for (A) control panel and (B) panel containing 50 P-DGEBA/50 EPON 825 resin system.

Table 3
Composite and neat resin density results as measured by water displacement.

Matrix composition[1]	Autoclave run #	Sample #	Composite ρ_c (g/cm^3)	Composite average	Sample #	Matrix ρ_R (g/cm^3)	Matrix average
Baseline (no P-DGEBA)	1	1	1.4472	1.453	1	1.1321	1.132
		2	1.4507		2	1.1311	
		3	1.4614		3	1.1317	
	2	1	1.4672	1.476	1	1.1414	1.142
		2	1.4710		2	1.1363	
		3	1.4890		3	1.1488	
	3	1	1.4458	1.461	1	1.1374	1.137
		2	1.4870		2	1.1358	
		3	1.4492		3	1.1378	
50/50 P-DGEBA /EPON 825	4	1	1.4980	1.491	1	1.1666	1.173
		2	1.4909		2	1.1836	
		3	1.4829		3	1.1687	

[1] Matrix comprised of epoxy monomer(s) at 69 wt% and EPIKURE 3274 at 31 wt%.

Table 4
Fiber volume fraction (Vf) calculations.

Matrix composition[1]	V_f using density from water submersion			V_f using panel thickness	
	Panel $\rho_{avg.}$ (g/cm^3)	Matrix $\rho_{avg.}$ (g/cm^3)	V_f (via Eq. (1))	CPT$_{avg.}$ (cm/ply)	V_f (via Eq. (2))
Baseline (no P-DGEBA)	1.463	1.137	0.507	0.02177	0.498
50/50 P-DGEBA /EPON 825	1.491	1.173	0.524	0.02181	0.497

[1] Matrix comprised of epoxy monomer(s) at 69 wt% and EPIKURE 3274 at 31 wt%.

and an estimated resin volume fraction of 0.5, the P-DGEBA containing composites were predicted to be 1.6% denser than the control panels, which is close the value obtained (1.9% denser).

The density results were used as the initial estimate of fiber volume fraction V_f using Eq. (1). The results are summarized in Table 4. The baseline panel had a V_f of 0.507, which is very close to the target value of 0.500 expected from the ratio of carbon fiber and resin used. The panel containing P-DGEBA had a significantly higher V_f at 0.524. To check these values, thickness measurements taken from each panel were used to calculate cured ply thickness (CPT), and then CPT was used to estimate V_f according to Eq. (2). The average thicknesses of the three baseline panels and the panel containing P-DGEBA were not significantly different, therefore the V_f calculated by this method were also very similar. Furthermore, the value obtained was approximately 0.5, which was the expected target value. Thus, the results point to the conclusion that the composite fiber volume fraction is around 0.5 as planned, but the high V_f value for the P-DGEBA sample obtained from density measurement remains unresolved. The density values were obtained from only three small pieces of the composite (not the entire panel) and small pieces of resin flash, so there is some inherent uncertainty in their values. In contrast, the panel average thickness values were obtained from 8 separate measurements of *each* 8.9 cm x 8.9 cm cone calorimeter coupon, and these indicated the panel thicknesses were the same which was expected since the panels were produced under the same conditions. At this point, it was concluded that the panel fabrication procedure was successful and produced panels representative of aerospace quality with a V_f around 0.5, which is an acceptable result for a panel fabricated form a woven carbon fabric.

The dynamic mechanical analysis (DMA) results for the composite coupons are discussed next. Fig. 9 shows typical curves, and the numerical results are summarized in Table 5. Three composite coupons each for baseline and P-DGEBA were tested. The average T_g for the baseline panel was 72 °C from the tan δ curve, while the T_g of P-DGEBA-containing panels climbed to 82 °C. This increase is consistent with DSC results for neat resin samples (Table 1), in which the 50/50 P-DGEBA/EPON 825 formulation exhibited a T_g over 10 °C higher than the baseline resin. It is suspected that the presence of the phosphorus atom restricts rotation more than the CH_3 group it replaces in the monomer core, thereby resulting in a small but noticeable increase in T_g. In addition, the high reactivity of P-DGEBA containing resin potentially provides the matrix with a higher crosslink density which would restrict segmental motions and also result in increased T_g. Geneally, the glass transition temperature (T_g) is considered to be one of the most crucial

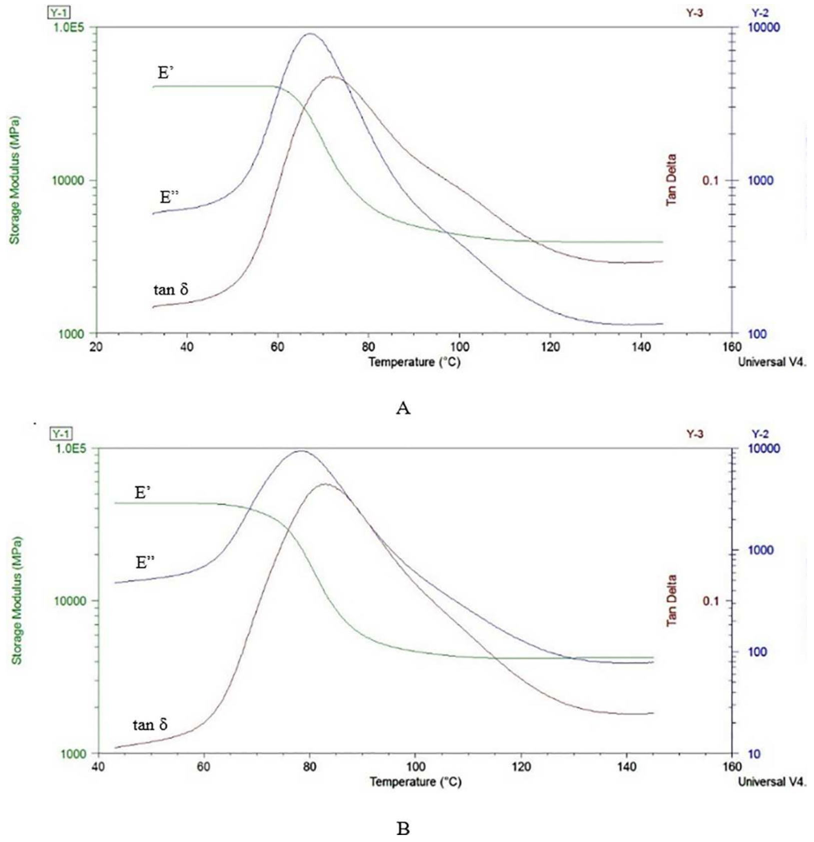


Fig. 9. Typical DMA curves for composites containing the (A) baseline epoxy resin system and (B) 50/50 P-DGEBA/DGEBA formulation.

Table 5
Composite panel T_g results using DMA.

Matrix composition[1]	Coupon #	T_g by Storage Modulus, E' (°C)	T_g by Loss Modulus, E'' (°C)	T_g by tan δ (°C)
Baseline (no P-DGEBA)	1	60.9	67.7	72.5
	2	62.0	67.3	72.3
	3	63.6	68.3	72.4
	Avg.	62.2	67.8	72.4
50/50 P-DGEBA /EPON 825	1	71.9	78.4	82.9
	2	71.3	78.3	83.0
	3	71.4	77.5	81.9
	Avg.	71.5	78.1	82.6

[1] Matrix comprised of epoxy monomer(s) at 69 wt% and EPIKURE 3274 at 31 wt%.

material characteristics of thermoset polymers used as composite matrices because it is strongly related to the upper use temperature and temperature-dependent mechanical properties [32].

3.4. Flammability results

3.4.1. Micro-combution calorimeter (MCC)

Table 6 summarizes the MCC results for the four neat resin samples (no carbon fibers), and it includes triplicate data to illustrate the repeatability of the measurements. The results include a polystyrene standard for comparison as per ASTM method. The MCC curves as well as the chars formed at the end of the test are given in Fig. 10. It is noticeable that when larger quantities of P-DGEBA were added to the epoxy samples, the total heat release and heat release rate dropped and the char production rose, strongly implying a condensed phase char formation reaction. Interestingly, when the P-DGEBA content was increased to 50% or greater, a secondary peak of heat release was observed, as can be seen in Fig. 10C and D. This could be due to an increase in the thermal decomposition of P-DGEBA independently of the base epoxy, resulting in an earlier peak of heat release as P-DGEBA decomposes and begins to char independently of the epoxy matrix. Fig. 10 clearly shows that peak HRR values were reduced compared to the base epoxy control sample (EPON 825), indicating that this particular epoxy co-monomer is acting as an efficient flame retardant to reduce heat release for epoxy. Overall, the MCC results indicate that the P-DGEBA lowered heat release and increased char yield. The 50% P-DGEBA formulation was selected as the optimum proportion in terms of balancing heat release reduction, increasing char production, and minimizing the amount of P-DGEBA required for making cone calorimeter plaques.

Table 6
Heat Release Rate (HRR) data for neat Epoxy/P-DGEBA + Epicure resin samples.

Sample	HRR Peak(s) Value (W/g)	HRR Peak(s) Temp (°C)	Total HR (KJ/g)	Char Yield (%)
0%P-DGEBA	514	399	25.2	5.66
	535	395	25.5	5.34
	547	401	25.3	5.30
75EPON/25 P-DGEBA	388	396	23.6	10.40
	375	390	24.1	10.46
	365	396	24.0	10.74
50 EPON/50 P-DGEBA	304, 246	351, 388	22.3	13.64
	304, 260	350,393	22.8	13.39
	258, 255	351, 393	22.6	13.18
25 EPON/75 P-DGEBA	278, 192, 49	332, 398, 475	20.5	15.86
	277, 192, 50	332, 398, 477	20.2	15.75
	269, 196, 48	332, 397, 477	21.1	16.3
PS standard	1046	444	39.1	0.06
	1057	444	39.3	0.03
	1075	445	39.2	0.05

When comparing the MCC (Table 6, Fig. 10) to the TGA data (Fig. 6

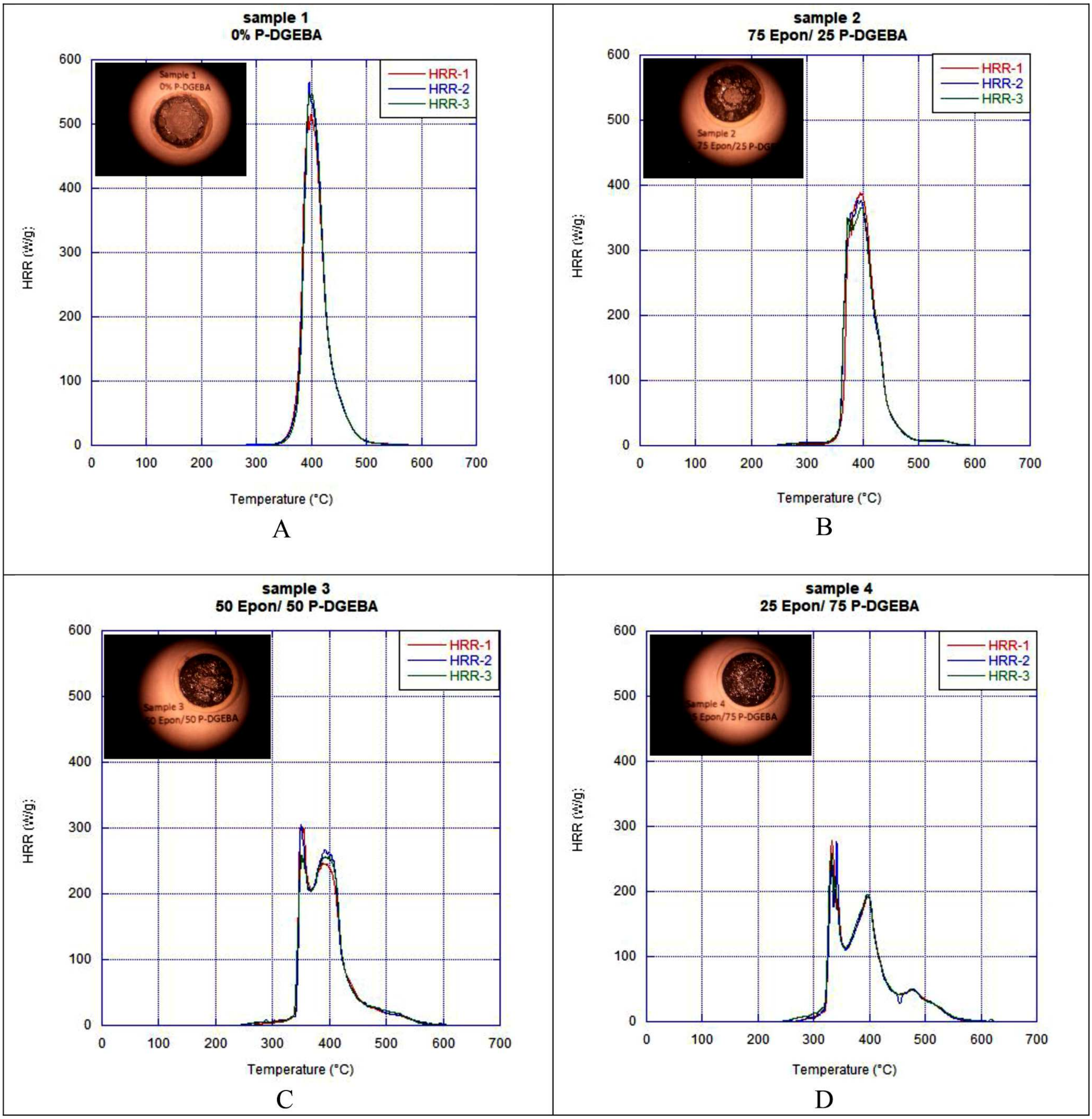


Fig. 10. Heat release curve and char picture for: (A) Baseline resin, (B) 75 EPON 825 / 25 P-DGEBA, (C) 50 EPON 825/50 P-DGEBA, and (D) 25 EPON 825 / 75 P-DGEBA.

Table 7
Cone calorimeter summary data.

Sample Description	Time to ignition (s)	Peak HRR (kW/m^2)	Time-to-Peak HRR (s)	Average HRR (Kw/m^2)	Weight Lost (%)	Total Heat Release (MJ/m^2)	Avg. effective heat of comb. (MJ/kg)	MARHE (kW/m^2)	Total Smoke Release (m^2/m^2)
Baseline EPON825/ Epikure3274	45	625	96	426	36.9	44.6	27.43	548	1746
	45	634	90	448	38.0	45.2	26.88	566	1695
	47	662	97	452	38.8	50.4	28.66	604	1765
Avg.	45	640	94	442	37.9	46.7	27.66	573	1735
P-DGEBA/ EPON825/ Epikure3274	41	462	87	339	38.0	33.7	19.79	439	2097
	37	486	90	337	40.0	38.3	20.11	478	2471
	43	434	77	333	34.1	28.4	19.91	394	1757
Avg.	40	460	85	336	37.5	33.5	19.94	437	2108

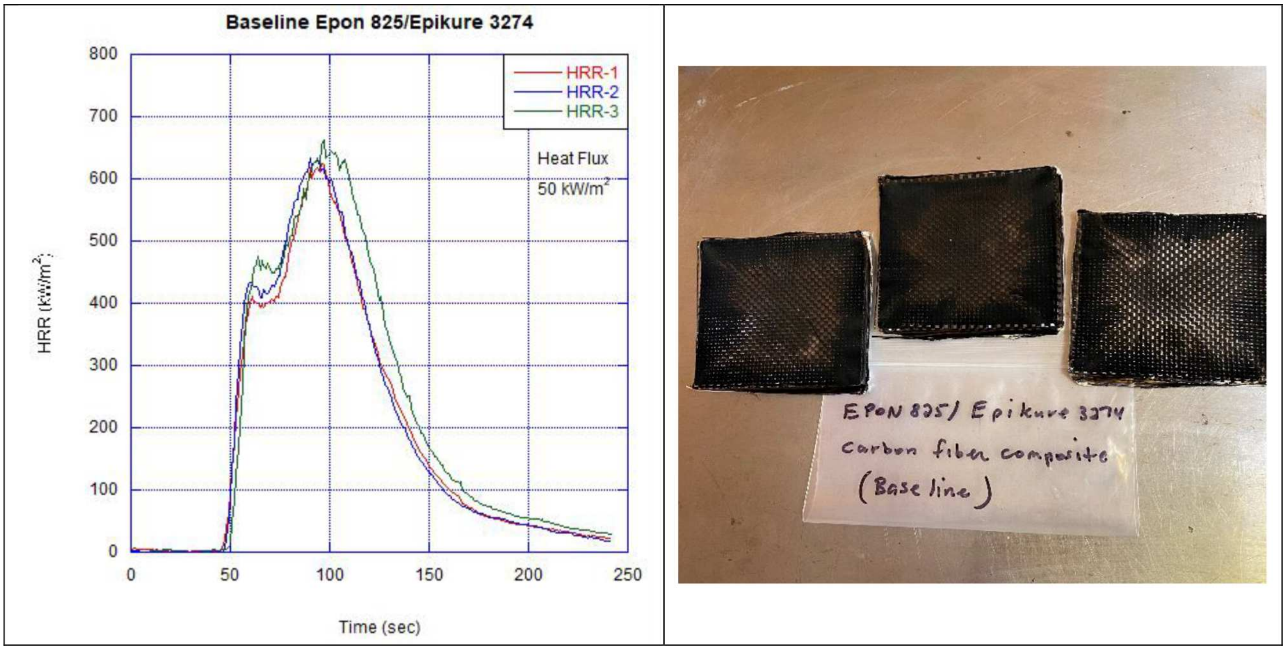


Fig. 11. Heat Release Rate (HRR) curve (left) and char picture (right) for sample control (EPON 825/Epikure 3274).

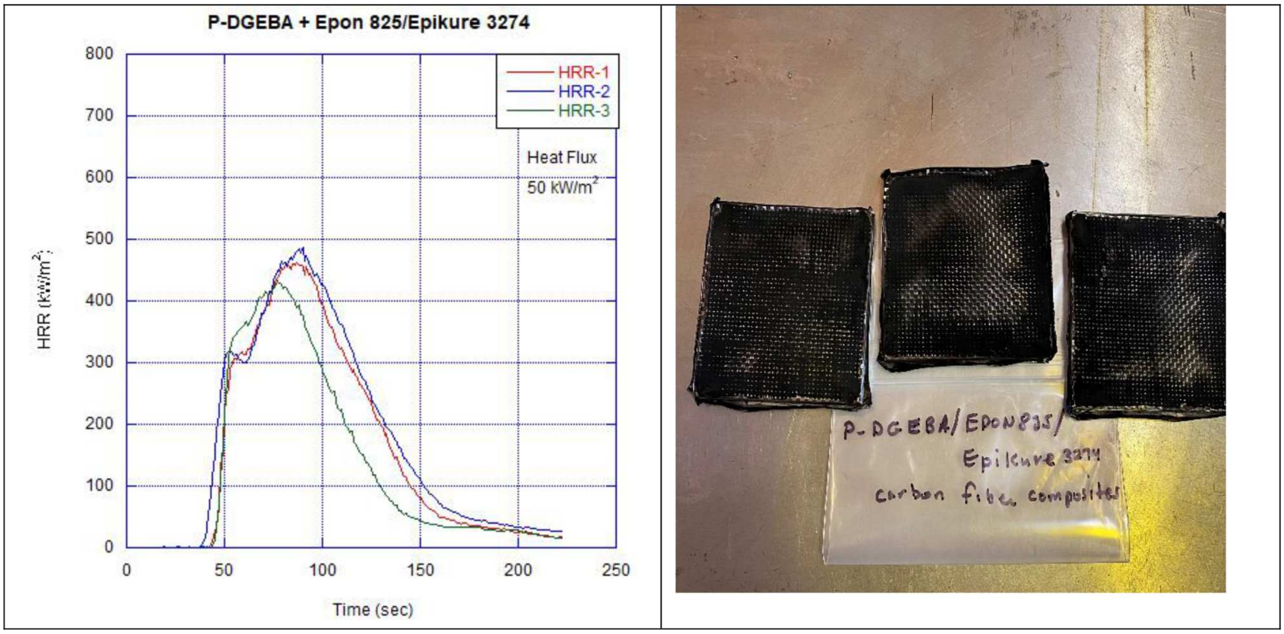


Fig. 12. Heat Release Rate (HRR) curve (left) and char picture (right) for sample P-DGEBA + EPON 825/Epikure 3274.

and Table 2), it is observed that the decomposition chemistry changes as increasing levels of P-DGEBA is added to the material. Specifically, with only 25% P-DGEBA, the decomposition intensity (HRR) is decreased (compare Fig. 10A and Fig. 10B), but it occurs over one broad temperature event. As P-DGEBA levels increase to 50 and 75% (compare Fig. 10C and Fig. 10D–A) one begins to observe two distinct heat release events at ~350 °C and 400 °C, with the peak of heat release at 350 °C moving to earlier temperatures as the onset of decomposition decreases as observed in the TGA results. Very likely, with increase P-DGEBA loading, the phenyl-phosphorus (C-P=O) bonds are beginning to break in higher and higher amounts and some radical recombination is occurring which generates higher levels of char. Based upon bond strengths, it can be hypothesized that the peak around 350 °C corresponds to C-P bond breaking and release of those corresponding flammable fragments from that first thermal decomposition step. It can be further hypothesized that the second peak around 400 °C corresponds to the rest of the DGEBA bonds breaking and pyrolyzing, with a third peak around 475 °C (Fig. 10D) likely corresponding to char formation from radical recombinations. Due to limited material and limited resources for this project, evolved gas analysis was not possible to confirm this hypothesis, but given known bond strengths in DGEBA and P-DGEBA, this hypothesis is a reasonable explanation for the results obtained.

3.4.2. *Cone calorimeter results*

The cone calorimeter results are summarized in Table 7, while the graphs are given in Figs. 11 and 12. Smoke started to form around 10 s after being exposed to the cone heater. At around 40 s, there was cracking and delamination noted for the composites right before ignition. Both formulations (baseline and the 50/50 sample) ignited around 40–45 s with total burn times under 3 min. HRR values were lower in the group containing P-DGEBA, while smoke values were higher. The final chars had a similar appearance due to the addition of some black ash to the fiber weave as shown in Figs. 11 and 12.

The results presented in Table 7 indicate that the char yields are mostly constant across the samples; however, the P-DGEBA exhibited lower heat release while increasing smoke production and decreasing effective heat of combustion. This implies that P-DGEBA is primarily a vapor phase flame retardant which produces condensed phase (char formation) behavior during combustion. It is interesting that the reduction in total heat release in MCC was only about 12% (50/50 neat resin sample) but was almost 40% for the cone calorimeter using a composite sample with 50% resin content. On the other hand, the char yield for MCC was promising (and was very similar to TGA), but there was no gain in char yield for the cone calorimeter results. The reduction in the heat release rates were also significantly better for cone calorimeter compared to MCC. The discrepancy between MCC and cone calorimeter results has been noted before, and the effect of high carbon fiber content interfering with char formation in the cone calorimeter samples cannot be ruled out [28]. However, it's more likely that in a forced combustion scenario like that of the cone calorimeter, P-DGEBA takes on more of a vapor phase flame retardant effect, while in a pyrolysis dominated decomposition scenario (PCFC), the effect is predominantly condensed phase. Most likely, there is some char formation occurring while the sample burns in the cone calorimeter, but the higher heat flux and constant ventilation of the cone calorimeter results in the P-DGEBA and its forming char to be pyrolyzed away into the combustion gases of the epoxy sample. When this happens, the P-DGEBA inhibits combustion, thus increasing smoke, reducing heat release, and lowering average effective heat of combustion.

4. Conclusions

Two chemical synthesis routes were developed to produce a phosphorous containing analog to DGEBA, referred to as P-DGEBA. While both led to the same compound, the second route was more efficient and is therefore recommended for future use. A total of approximately 25 g of P-DGEBA were produced from both routes. Studies of P-DGEBA revealed that the material was a low-melting solid, which eased manupulation in the process of producing reinforced composites. Additionally, since the P-DGEBA/DGEBA blend had similar rheology to other liquid epoxy resin products, the formulation and mixing process was successfully done without the need for heating or special mixing conditions. In addition, a process was developed to fabricate high quality carbon fabric composite laminates with a fiber volume fraction of 0.5 with little or no waste of the scarce amount of P-DGEBA available. The matrix of these composites contained a 50/50 wt%/wt% blend of DGEBA and P-DGEBA as the epoxy component, and a stoichiometric amount of the curing agent. DMA study of composite coupons revealed that the T_g of the baseline panel was 72 °C, while the T_g of panels containing P-DGEBA was about 10 °C higher. This indicates that P-DGEBA does not lower the effective use temperature of the composite once incorporated into the epoxy. The TGA, MCC and Cone Calorimeter tests give somewhat conflicting answers in regards to the flame retadrant mechanism/mode of action of P-DGEBA. All tests show heat release reduction, but TGA and MCC show this to be a mostly condensed phase/char formation effect, while cone calorimeter suggests a mostly vapor phase effect. Very likely, P-DGEBA is both, but in flaming forced combustion modes (like those seen in the cone calorimeter) [28], it is for all practical purposes a vapor phase flame retadrant, even though it may form some char prior to being transported to, and consumed in the flame front of a fire event. P-DGEBA therefore shows promise as an effective reactive flame retadant for epoxy in that it maintains mechanical properties, increases T_g, and decreases heat release. Further studies of combinining P-DGEBA with other epoxies or other reactive flame retadrants to lower heat release further would be a useful area of research. Mechanical property testing, which is often needed for carbon-fiber based composites, was not conducted in this study due to funding limitations, and would need to be studied in the future to determine if P-DGEBA also brings a good balance of properties to the composite material. Additionally, comparing P-DGEBA to other commercial phosphorus-based FRs (such as DOPO) with carbon fibers at the same carbon fiber loading would be a good topic to study further to determine if the P-DGEBA provides equivalent or superior/inferior fire performance vs. the commercialized material.

CRediT authorship contribution statement

Mustafa Mukhtar: Investigation, Formal analysis, Data curation, Writing – original draft. **Donald Klosterman:** Methodology, Formal analysis, Data curation, Writing – original draft. **Vladimir Benin:** Methodology, Data curation, Formal analysis, Writing – original draft. **Alexander Morgan:** Project administration, Methodology, Formal analysis, Data curation, Writing – original draft.

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.

Data Availability

The data that has been used is confidential.

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Supplementary materials

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