

Synthesis and flammability testing of epoxy functionalized phosphorous-based flame retardants

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ABSTRACT: Several potential new phosphorus-containing flame retardant molecules were evaluated for heat release reduction potential by incorporation of the molecules into a polyurethane, generated from methylene diphenyl diisocyanate and 1,3-propane diol. The heat release reduction potential of these substances was evaluated using the pyrolysis combustion flow calorimeter (PCFC). The polyurethanes were prepared in the presence of the potential flame retardants via solvent mixing and copolymerization methods to qualitatively evaluate their potential reactivity into the polyurethane prior to heat release testing. The functionality of the flame retardants was epoxide based that would potentially react with the diol during polyurethane synthesis. Flammability testing via PCFC showed that the heat release reduction potential of each of the flame retardants was structure dependent, with phosphates tending to show more effectiveness than phosphonates in this study, and alkyl functionalized phosphorus groups (phosphate or phosphonate) being more effective at heat release reduction than cyclic functionalized groups. © 2015 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2015**, *132*, 42296.

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INTRODUCTION

The use of flame retardants to provide fire protection for polymeric materials is a well-proven and used method in the present society. There are a variety of chemistries and approaches available, and numerous good books and review articles on the subject.^{1–4} Use of said additives, however, is not so simple that it can be added to any material when a fire risk is identified. When the need for flame retardants has been identified, there are two major requirements to consider based upon the current knowledge of fire safety and environmental/product lifetime needs. First is that the flame retardant works to provide protection against a specific fire risk scenario. Second is that the flame retardant do not leach out of the product over time. Therefore, new flame retardants for potential use must be screened not only for flame retardant performance but also for their potential reactivity into a polymer. While screening for the first requirement, fire performance, can be done via a variety of methods depending upon the scale of available flame retardant and end-use application,^{2–4} screening for the second requirement can take a bit more effort when one considers the complexity of various manufacturing processes and product end-of-life issues. Therefore, one should screen for fire performance first to make

sure that there is at least some potential value as a flame retardant in a new chemical structure. Once flame retardant potential has been assessed, fine-tuning of chemical structure that works as a reactive flame retardant in a particular polymer can be undertaken.

In a previous study, we reported upon the synthesis and testing of new boron and phosphorus-based flame retardants as potential reactive flame retardants for polyurethane foam.⁵ In continuation of that work, we are studying new phosphorus-containing molecules as potential reactive flame retardants for polyurethanes. Phosphates and phosphonates are known to work as flame retardants in a variety of polymers,^{2,4,6} but flame retardant effectiveness can vary depending upon the chemical structure of the organophosphorus compound and how it reacts into the polymer structure during polymer synthesis. Chemistry can be tailored for the phosphorus-based flame retardant to react into the polymer during synthesis and, for example, this has been done for thermoplastic polyurethanes and methacrylate polymers.^{7–9} Further, phosphorus is an attractive target for polyurethane flame retardancy due to its potential to lower heat release through char formation,^{1,2,4–6} and lowering heat release is a known target for improving polyurethane fire safety.^{10,11} In

this report, we focus on epoxy functionalized phosphates and phosphonates. The epoxy compounds have some potential as reactive flame retardants in polyurethane via the hydroxyl groups in polyurethane polyols reacting with the epoxides to make flame retardant polyols that in turn react with isocyanates. Returning to the concept that screening for fire performance should come first, in this article, we report exploratory studies only on the fire performance of the additives when mixed with polyurethanes via *in-situ* polymerization, with experiments also carried out on samples where the flame retardant was incorporated via solvent blending to see if the flame retardant is more or less effective at reducing heat release when not chemically reacted into the polyurethane. Fire performance was screened for heat release reduction potential via pyrolysis combustion flow calorimetry (PCFC), a proven tool for flame retardant screening.^{12–17} Some discussion on the flame retardant potential and mechanism is included, but it must be cautioned that due to the limited data in this article, we can only infer mechanism and reaction into the polyurethane.

EXPERIMENTAL

General Procedures and Chemicals

¹H and ¹³C spectra were recorded at 300 and 75 MHz, respectively, and referenced to the solvent (CDCl₃: 7.27 and 77.0 ppm; DMSO-*d*₆: 2.49 and 39.5 ppm). ³¹P NMR spectra were measured at 121 MHz and referenced to H₃PO₄ solution in DMSO-*d*₆ (0.0 ppm) or a (CH₃O)₃P solution in CDCl₃ (141.0 ppm). The referencing 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. P-Elemental analysis was provided by Galbraith Laboratories, Inc., Knoxville, TN.

Compounds **1a**,¹⁸ **2a**,¹⁸ and **8a**¹⁹ have been previously prepared, characterized, and reported in the literature. Their synthesis is therefore not described in this article. Compounds **5**^{20,21} and **8b**, although previously reported,²² were prepared following modified protocols. Their synthesis is therefore described in detail.

Synthesized Flame Retardants

2-Methoxy-5,5-dimethyl-1,3,2-dioxaphosphinane (5). A mixture of 2,2-dimethyl-1,3-propanediol (12.00 g, 115 mmol) and trimethyl phosphite (13.04 g, 105 mmol, 12.40 mL) was stirred at 100°C, and a simple distillation apparatus was used to collect the resultant methanol. After the end of methanol evolution, the residue was purified through fractional vacuum distillation, with a bath temperature of 125°C and pressure of 0.1 mm Hg. The desired fraction distilled at 40–45°C, giving 2.74 g (16%) of product as a colorless liquid. ¹H NMR (CDCl₃) δ 0.73 (s, 3H), 1.25 (s, 3H), 3.30 (t, *J* = 21.1 Hz, 2H), 3.54 (d, *J* = 11.9 Hz, 3H), 4.10 (d, *J* = 11.6 Hz, 2H).

2-Oxo-2-allyl-5,5-dimethyl-1,3,2-dioxaphosphinane (6).

Method 1. A mixture of allyl bromide (0.84 g, 6.93 mmol, 0.60 mL) and 2-methoxy-5,5-dimethyl-1,3,2-dioxaphosphinane (1.00 g, 6.10 mmol) was stirred at 130–140°C for 4 h. The remaining allyl bromide was removed under vacuum. The

residue was recrystallized by dissolving it in a 1 : 1 mixture of toluene and hexane at ambient temperature, followed by 24 h at –25°C. The resultant solid was filtered to yield 0.76 g (66%) of the target compound. Mp 111–113°C. ¹H NMR (CDCl₃) δ 0.92 (s, 3H), 1.05 (s, 3H), 2.65 (ddt, *J*₁ = 22.0 Hz, *J*₂ = 7.4 Hz, *J*₃ = 2.4 Hz, 2H), 3.75 (dd, *J*₁ = 15.6 Hz, *J*₂ = 11.2 Hz, 2H), 4.14 (dd, *J*₁ = 11.1 Hz, *J*₂ = 6.9 Hz, 2H), 5.14–5.23 (m, 2H), 5.75 (m, 1H). ¹³C NMR (CDCl₃) δ 21.1, 21.4, 30.0 (d, *J* = 36.7 Hz), 32.4 (d, *J* = 6.0 Hz), 74.7 (d, *J* = 6.4 Hz), 120.3 (d, *J* = 14.4 Hz), 126.4 (d, *J* = 11.6 Hz). ³¹P NMR (CDCl₃) δ 23.6 (s, 1P). Anal. Calcd. for C₈H₁₅O₃P: C, 50.52; H, 7.95. Found: C, 50.57; H, 7.77.

Method 2. Sodium hydride (0.20 g, 8.12 mmol) was suspended in dry THF (5 mL). The suspension was cooled to –78°C (dry ice–acetone) and 2*H*–5,5-dimethyl-1,3,2-dioxaphosphane (**4**) (1.11 g, 7.38 mmol), dissolved in dry THF (10 mL), was added over a 10 min period. The mixture was stirred at the same temperature for 1 h, and then allyl bromide (0.89 g, 7.38 mmol, 0.64 mL) was added. The mixture was allowed to warm up gradually to ambient temperature and stirred for 12 h, followed by reflux for 3 h. Solids were separated via vacuum filtration. The filtrate was concentrated under reduced pressure, leaving an oily residue that slowly solidifies. NMR is identical with that generated by the product from Method 1.

2-Oxo-2-(2,3-epoxypropyl)-5,5-dimethyl-1,3,2-dioxaphosphinane

(1b). 2-Oxo-2-allyl-5,5-dimethyl-1,3,2-dioxaphosphinane (0.69 g, 3.63 mmol) was dissolved in chloroform (10 mL), and *meta*-chloroperbenzoic acid (MCPBA) (0.63 g, 3.63 mmol) was added to the solution over 20 min at 0–5°C. The solution was stirred at ambient temperature for 5 h, after which more MCPBA (0.32 g, 1.81 mmol) was added. Stirring was continued for 12 h at ambient temperature, followed by 6 h at reflux. The solution was cooled and washed twice with 50 mL of saturated aq. Na₂CO₃, once with 25 mL of a saturated aq. Na₂S₂O₃, followed by water. The organic layer was dried (MgSO₄) and the solvent was removed under reduced pressure to give 0.35 g (47%) of the product as a white solid. Mp 57–59°C. ¹H NMR (CDCl₃) δ 0.95 (s, 3H), 1.06 (s, 3H), 1.94 (ddd, *J*₁ = 20.1 Hz, *J*₂ = 15.5 Hz, *J*₃ = 6.3 Hz, 1H), 2.23 (ddd, *J*₁ = 18.1 Hz, *J*₂ = 15.4 Hz, *J*₃ = 5.9 Hz, 1H), 2.55 (dd, *J*₁ = 2.5 Hz, *J*₂ = 4.8 Hz, 1H), 2.79 (m, 1H), 3.16 (m, 1H), 3.80 (m, 2H), 4.16 (m, 2H). ¹³C NMR (CDCl₃) δ 21.1, 21.4, 28.6 (d, *J* = 136.0 Hz), 32.4 (d, *J* = 5.9 Hz), 46.2 (d, *J* = 2.6 Hz), 47.1 (d, *J* = 7.7 Hz), 74.8 (d, *J* = 6.3 Hz), 74.9 (d, *J* = 6.4 Hz). ³¹P NMR (CDCl₃) δ 22.9 (s, 1P). Anal. Calcd. for C₈H₁₅O₄P: C, 46.60; H, 7.33. Found: C, 46.85; H, 7.42.

2-Oxo-2-allyloxy-5,5-dimethyl-1,3,2-dioxaphosphinane (8b).

Sodium hydride (0.53 g, 22.06 mmol) was suspended in dry THF (15 mL) and allyl alcohol (1.28 g, 22.06 mmol, 3.00 mL) was added dropwise to the suspension over 15 min period. After stirring for additional 15 min, 2-chloro-2-oxo-5,5-dimethyl-1,3,2-dioxaphosphane (4.07 g, 22.06 mmol), dissolved in dry THF (20 mL), was added dropwise and the resultant mixture was stirred for 12 h at ambient temperature, followed by 4 h at reflux. The solvent was removed under reduced pressure and the residue was treated with methylene chloride and water. The organic layer was separated, dried (MgSO₄), and the

solvent removed under reduced pressure, yielding the product as a white solid (2.50 g, 55%). ^1H NMR (CDCl_3) δ 0.87 (s, 3H), 1.23 (s, 3H), 3.90 (dd, $J_1 = 9.0$ Hz, $J_2 = 18.0$ Hz, 2H), 4.07 (dd, $J_1 = 3.0$ Hz, $J_2 = 9.0$ Hz, 2H), 4.50–4.59 (m, 2H), 5.21–5.41 (m, 2H), 5.85–6.02 (m, 1H).

2-Oxo-5,5-dimethyl-2-[(2-oxiranyl)methoxy]-1,3,2-dioxaphosphinane (2b). 2-Oxo-2-allyloxy-5,5-dimethyl-1,3,2-dioxaphosphinane **8b** (0.53 g, 2.57 mmol) was dissolved in chloroform (10 mL), and MCPBA (0.45 g, 2.57 mmol) was added to the solution over 20 min at 0–5°C. The solution was stirred at ambient temperature for 5 h, after which more MCPBA (0.23 g, 1.29 mmol) was added. Stirring was continued for 12 h at ambient temperature, followed by 6 h at reflux. The solution was cooled and washed twice with 50 mL of saturated aq. Na_2CO_3 , once with 25 mL of saturated aq. $\text{Na}_2\text{S}_2\text{O}_3$, followed by water. The organic layer was dried (MgSO_4) and the solvent was removed under reduced pressure to give 0.46 g (80%) of the product as a white solid. Purification via column chromatography (acetone : hexane = 3 : 1). Analytical samples were obtained via recrystallization from toluene/hexane mixture. Mp 48–50°C. ^1H NMR (CDCl_3) δ 0.87 (s, 3H), 1.25 (s, 3H), 2.68 (dd, $J_1 = 2.6$ Hz, $J_2 = 4.8$ Hz, 1H), 2.86 (t, $J = 4.5$ Hz, 1H), 3.24–3.28 (m, 1H), 3.84–3.95 (m, 3H), 4.14 (td, $J_1 = 2.3$ Hz, $J_2 = 10.5$ Hz, 2H), 4.39 (ddd, $J_1 = 2.7$ Hz, $J_2 = 7.3$ Hz, $J_3 = 11.8$ Hz, 1H). ^{13}C NMR (CDCl_3) δ 20.2 (d, $J = 0.8$ Hz), 21.6, 32.0 (d, $J = 5.9$ Hz), 44.4, 49.9 (d, $J = 7.5$ Hz), 67.5 (d, $J = 5.2$ Hz), 77.9 (dd, $J_1 = 2.8$ Hz, $J_2 = 6.8$ Hz). ^{31}P NMR (CDCl_3) δ 7.97 (s, 1P). Anal. Calcd. for $\text{C}_8\text{H}_{15}\text{O}_5\text{P}$: C, 43.25; H, 6.81. Found: C, 43.27; H, 6.68.

Bis(oxiran-2-ylmethyl) (2-oxo-1,3-dioxolan-4-yl)methyl phosphate (3). Phosphoryl chloride (16.44 g, 107.20 mmol, 10.00 mL) was dissolved in dry THF (150 mL) and the solution was cooled to –78°C (dry ice–acetone). A solution of glycerol carbonate (12.66 g, 107.20 mmol, 9.04 mL) and triethylamine (10.86 g, 107.20 mmol, 14.96 mL) in dry THF (150 mL) was added dropwise over 2 h period, at the same temperature. The mixture was then allowed to gradually warm up to room temperature and stirred for additional 12 h. The solvent was removed under reduced pressure to yield (2-oxo-1,3-dioxolan-4-yl)methyl phosphorodichloridate (**10**) as a dark solid, which was used without further purification.

Glycidol (4.42 g, 59.64 mmol, 3.98 mL) and triethylamine (6.04 g, 59.64 mmol, 8.32 mL) were dissolved in dry THF (50 mL) and the solution cooled to 0–5°C (ice–water bath). A solution of compound **10** (6.65 g, 28.30 mmol) in dry THF (50 mL) was added dropwise over 0.5 h period. The solution was allowed to warm up to ambient temperature and stirred for additional 12 h. The reaction mixture was vacuum filtered and the filtrate was concentrated under reduced pressure. The residue was treated with ether/water, the organic layer was separated, dried (MgSO_4), and the solvent was removed to yield the product **3** as a dark yellow oil (1.23 g, 14%). Further purification was achieved by flash chromatography on a short silica gel column. Elution was conducted with ethyl acetate, followed by acetonitrile. The latter fractions were collected and the solvent evaporated to yield a colorless oil. ^1H NMR (CDCl_3)

δ 2.67–2.70 (m, 2H), 2.86 (t, $J = 4.3$ Hz, 2H), 3.24–3.28 (m, 2H), 3.93–3.97 (m, 2H), 4.20–4.28 (m, 1H), 4.36–4.47 (m, 4H), 4.57 (t, $J = 8.7$ Hz, 1H), 4.91–4.97 (m, 1H). ^{13}C NMR (CDCl_3) δ 44.3 (d, $J = 6.2$ Hz), 44.4 (bs), 49.8 (d, $J = 28.7$ Hz), 65.5 (bs), 66.2 (d, $J = 21.0$ Hz), 68.8 (d, $J = 22.8$ Hz), 74.0 (d, $J = 30.8$ Hz), 154.3. ^{31}P NMR (CDCl_3) δ 1.4 (s), 1.3 (s), and 1.2 (s). Anal. Calcd. for $\text{C}_{10}\text{H}_{15}\text{O}_5\text{P}$: C, 38.72; H, 4.87. Found: C, 39.05; H, 5.04.

Polyurethane Synthesis

Sample preparation of polyurethane samples was modified from previously published work,²³ and is otherwise identical to procedures in one of our previous publications.⁵ Still, for the purposes of experimental clarity, the method is described here. To assist the readers in understanding how the flame retardant was incorporated into the samples, two definitions of “Prep” and “Blend” are used. Samples labeled “Prep” incorporated the flame retardant (FR) at 10 mol % during the polymerization process (the FR was present with the monomers during the polymerization reaction). Samples labeled “Blend” incorporated the FR at 10 mol % via solvent blending of FR and polyurethane after the polyurethane was already synthesized. “Prep” samples have the potential for the FR to react into the polymer, but also be washed out if not fully reacted in, and the “Blend” samples will always have the full loading of FR additive, but it will not be chemically incorporated into the polymer structure.

Heat Release Testing

The polyurethane samples were measured for heat release using PCFC via ASTM D7309-07, Method A (pyrolysis under nitrogen) with a heating rate of 1°C/s and heating of the sample from 175 to 800°C. Testing was conducted in triplicate as per the ASTM method.

RESULTS AND DISCUSSION

Synthesis

The structures investigated and reported in this article were composed of epoxy-containing phosphonates and phosphates which are shown in Figure 1. Phosphonate **1a** was prepared following a literature protocol, from trimethylphosphite and epibromohydrin, in conditions typical for the Michaelis–Arbuzov reaction (Scheme 1).^{18,24} The same strategy was not successful in the case of **1b**, leading actually to polymerization. It necessitated the implementation of a stepwise protocol, *via* the corresponding allyl phosphonate ester **6**. The latter was successfully derived from either the cyclic dialkylphosphite **4**^{25,26} or the trialkylphosphite **5**, then epoxidized to the target structure **1b** using MCPBA. Originally, we conducted the epoxidation process at ambient temperature, in THF, following the procedure of Perie *et al.*¹⁸ However, the product mixtures contained large amounts of unreacted starting material. Subsequently, we adopted a protocol that combined stirring at both ambient temperature and reflux. The solvent was changed from THF to chloroform.²²

Epoxyphosphates too can be prepared following two general strategies. The first is a direct reaction of glycidol with a chlorophosphate, while the second is a two-step protocol, which involves formation of an allyl ester, followed by epoxidation.

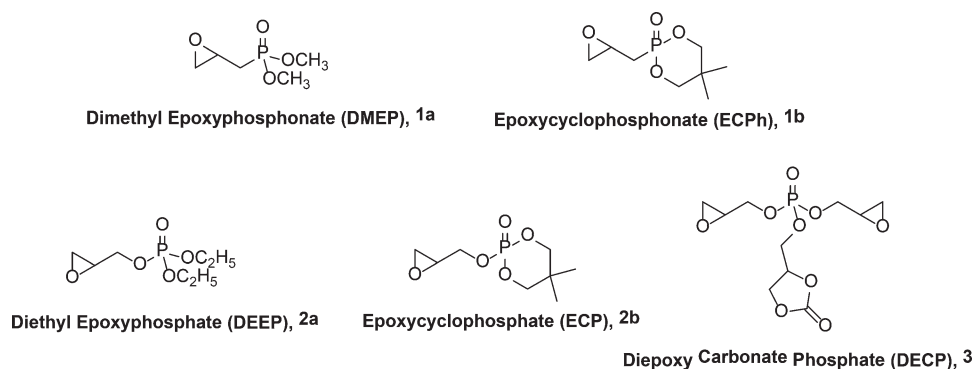


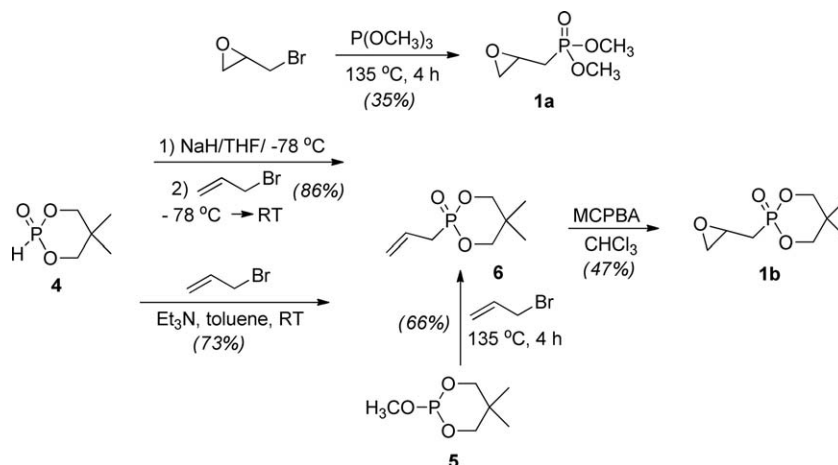
Figure 1. Target epoxy-containing phosphonate and phosphate structures.

So far, we have found the second strategy to be more generally applicable. Thus, using the appropriate chlorophosphates, we have managed to prepare the desired allyl phosphates **8a,b** (Scheme 2).^{19,22,27} Compound **8a** was prepared using previously described procedure, employing allyl alcohol and triethylamine base. The same approach, however, failed in the case of **8b**, in which case the starting material was isolated. The protocol was modified to involve preliminary deprotonation of allyl alcohol with NaH, followed by reaction of the chlorophosphate **9** with the resultant alkoxide. The epoxidation conditions, used for the preparation of **1b**, were implemented without change and have led to the successful preparation of targets **2a** and **2b**.

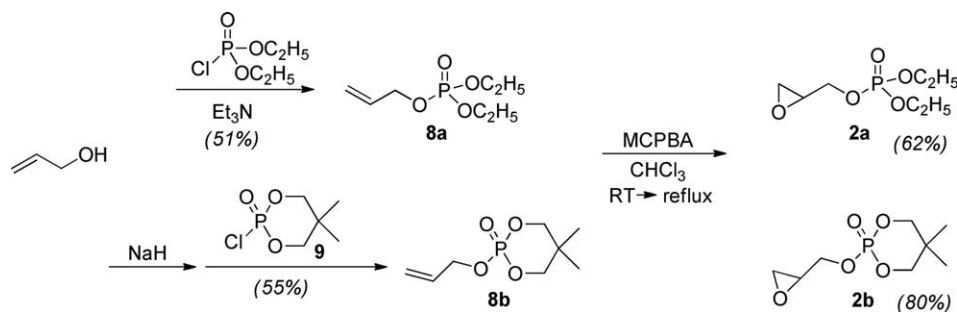
Attempts to utilize the one-step protocol starting with glycidol, and therefore directly introduce the epoxide functionality, have also been successful. Thus, we managed to conduct a single-step preparation of **2a**, from the corresponding chlorophosphate (Scheme 3). Following this approach, we have also managed recently to prepare a new epoxyphosphate **3** that contains two epoxide functionalities and a glycerol carbonate moiety.²⁸ The starting dichlorophosphate **10** was prepared using a modified literature protocol, from glycerol carbonate and phosphoryl chloride. NMR data on a pure sample of compound **3** seem to support the presence of several stereoisomers, stemming from the presence of three chirality centers in the structure.

NMR and Phosphorus Elemental Analysis Studies

All of the “Prep” samples were characterized using ¹H- and ³¹P-NMR spectroscopy to determine if the flame retardant was incorporated into the structure or not. Given the fact that the potential FR was used in relatively small quantities (10 mol %) and only some of it would be incorporated, the ¹H NMR spectra predictably failed to provide definitive information. More reliable are ³¹P data and those are summarized in Table I. As can be seen from the data, all studied samples showed some degree of incorporation of the FR, as evidenced by the presence and detection of a ³¹P signal in every case. The table also provides ³¹P data on the starting monomeric FR, and comparison clearly shows a difference in the NMR shifts and/or patterns between the monomer and the resultant PU sample with the FR included. This qualitatively indicates that the FR is incorporated into the polymer, but either the phosphorus structure has changed during polymer synthesis or the interaction between polymer and phosphorus FR has resulted in new chemical shifts in the ³¹P NMR signals. With the research tools available, we are not able to determine which is the case with the samples in this article, but, we can infer that in cases where the starting material had only one peak in the ³¹P NMR, and now multiple peaks are observed in the presence of the polymer, that the multiple peaks suggest reaction at the phosphorus atom. Specifically, the 1,3-propane diol may have transesterified with the



Scheme 1. Preparation of the epoxyphosphonates DMEP (**1a**) and ECPh (**1b**).



Scheme 2. Preparation of the epoxyphosphates DEEP (2a) and ECP (2b).

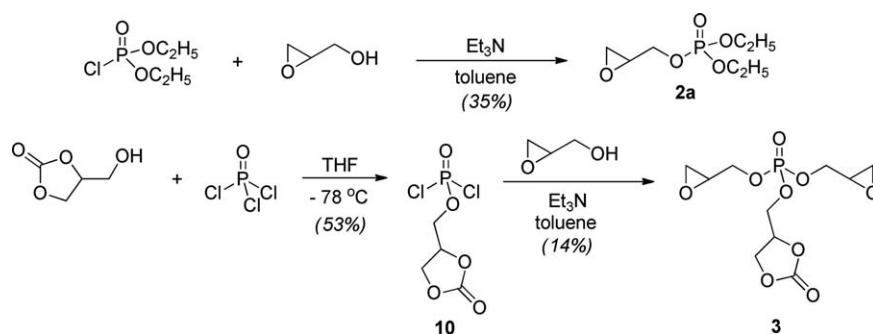
phosphorus esters in the cases of compounds ECPh, ECP, and DECP. However, we cannot rule out that complex interactions that occurred between epoxy functionality and urethanes, which would lead to even more complex chemical signatures in the NMR signal. We can at least infer reaction occurred, but at this time cannot say which reactions did or did not occur as the flame retardant reacted with the monomers during polymerization. Additional evidence for flame retardant incorporation comes from phosphorus elemental analysis data. Results were obtained using Inductively Coupled Plasma Atomic Emission spectrometry, following specifically the GLI procedure ME-70. All measurements were based on an initial run with an independent quality control source, against a 5-point calibration, which has to be within $\pm 10\%$ of the theory. Based on those results, we have estimated the percentage of FR, incorporated into the polyurethane. As evident from the results in Table II, all studied structures are incorporated into the polymer, i.e., can serve as reactive flame retardants. The degree of incorporation is greater for the acyclic epoxides DMEP and DEEP, which seems to correlate somewhat with the flammability results (*vide infra*).

Heat Release Results

Before discussing the PCFC data in detail, some discussion about the technique is needed. It should be noted that the PCFC is a very good tool for screening, but it may not always generate results that predict perfectly fire performance in full-scale fire tests. While there have been some notable advances in how the PCFC can predict performance in some larger scale tests,²⁹ fire performance that rely heavily upon physical behavior (example, drip-back away from the flame) will not be captured or observed correctly by the PCFC. Relevant for the fire safety goals of this article, screening for heat release reduction

potential will be useful for finding new materials that lower the heat release in polyurethane foam in furniture and bedding, but that same PCFC data may not predict “passing” results in existing fire safety tests where heat release is not a key focus of said test. Therefore, the reader of this article should keep in mind that what is presented in this article is heat release reduction potential, and complex fire phenomena like furniture construction, ventilation, and fire source will affect regulatory fire performance and the heat release reduction potential of the materials in this article is not a guarantee of successful fire performance in a regulatory test. Indeed, such a caveat is found in the ASTM D7309 standard.³⁰

The PU + “Prep” and “Blend” samples were analyzed for heat release reduction via PCFC. The model PU structure is shown in Figure 2, while Table II shows the measured and theoretical percentage of phosphorus for each of the PU samples. The percentage of phosphorus (%P) may be significant to the heat release reductions in that the phosphorus atom is the “active” part of the FR and from literature results, the more %P in the system, the more of a flame retardant effect is noted,^{2,4,6} but this is not always the case as how the phosphorus is incorporated into the FR chemical structure has an equally important flame retardant effect.^{4-6,31-34} It is important to note again that this % total P in each PU formulation is theoretical and assumes 100% reaction or presence in the final product. In the case of the “blend” samples, this total %P can be assumed to be present since the FR was not washed out after mixing with the model polyurethane. In the case of the “Prep” samples, where the FR was reacted in, this assumption cannot be made. The data in Table II, however, does show how much %P was incorporated into the sample, and while in each case there is less than a 100% reaction, there is still notable amounts of FR



Scheme 3. Preparation of the bis(epoxy)phosphate DECP (3).

Table I. ^{31}P NMR Data on PU Samples Prepared Using 10 mol % of FR

Compound	^{31}P NMR of pure FR	^{31}P NMR signals of PU samples, prepared with 10 mol % FR
DMEP, 1a	28.8 (sharp) ⁵	32.4 (sharp)
ECPH, 1b	22.9 (sharp)	20.9 (sharp), 23.7 (sharp), 30.9 (sharp), 31.0 (sharp)
DEEP, 2a	-1.0 (sharp) ⁵	-0.9 (sharp)
ECP, 2b	-8.0 (sharp)	-9.4 (sharp), -9.2 (sharp), -8.4 (sharp), -8.1 (sharp), -7.7 (sharp), -7.5 (sharp), -7.1 (sharp)
DECP, 3	-1.4 (sharp), -1.3 (sharp), -1.2 (sharp)	-9.0 (sharp), -8.9 (sharp), -8.5 (sharp), -8.1 (sharp), -7.6 (sharp), -7.3 (sharp), -6.6 (sharp), -0.9 (sharp), -0.8 (sharp). Also, several very broad signals in the region -10 to -4 ppm

All results from measurements on a 300 MHz Bruker NMR instrument (121 MHz resonance frequency for ^{31}P). ^{31}P signals referenced to H_3PO_4 dissolved in $\text{DMSO}-d_6$ (0.0 ppm). Chemical shifts in ppm.

incorporated. So in the “Prep” samples discussed in this report, it may not always be a perfect comparison between samples in regard to effectiveness because not all of the FR reacted into the polymer. On the other hand, if the amount of FR that actually incorporated into the polymer is the maximum possible due to limits of polymerization kinetics, steric hindrance, or other possible hypotheses, then the results, while not optimized or maximized for 100% FR incorporation, are still useful qualitative measurements of performance. In any case, the results show that not all reactive flame retardants are the same, and finding a reactive flame retardant with good flame retardant performance and good reaction potential is not an easy undertaking.

The control polyurethane of 1,3-propane diol and methylene diphenyl isocyanate (Figure 2) is shown for its heat release in each of the tables below. The heat release data for the PU + epoxy phosphonates is shown in Table III. In blend form, the epoxy phosphonates **1a** and **1b** have a negative effect on total heat release, suggesting that contribute to the total fuel load of the polyurethane. The epoxy phosphonates slightly increase the char yield of the polyurethane, but not greatly. When studying the heat release rate curves (Figure 3), the dimethyl phosphonate (**1a**) results in a higher initial peak HRR, and the cyclophosphonate (**1b**) lowers the initial peak HRR. This suggests that the dimethyl phosphonate (**1a**) is quickly volatilizing during initial pyrolysis, but some material remains behind to change the rest of the decomposition of the polyurethane, but not enough to result in a meaningful total HR reduction. The cyclophosphonate (**1b**), being higher molecular

weight, remains around longer to reduce some initial heat release, but does not remain in the polyurethane long enough to reduce total HR or result in meaningful char. In prep form, interestingly, the cyclophosphonate (**1b**) has practically no effect on heat release positive or negative (although initial peak HRR is increased) which may suggest that it did not react into the polyurethane at high levels during polymer synthesis and was washed out. Indeed, cyclophosphonate **1b** is soluble in methanol, the solvent used for washing the final “prep” polyurethane product. However, the ^{31}P NMR data does show multiple peaks, and so it is possible that cyclophosphonate **1b** has become chemically changed upon reacting into the PU, and when this occurs, most of its flame retardant effectiveness (at least from a heat release reduction perspective) is lost. Further, the elemental analysis results indicate that only 3.6 of the maximum 10 mol % of the FR actually reacted into the polymer, and therefore, the lack of reaction plus change in structure is likely the reason why there is little benefit from this particular FR structure.

The dimethyl phosphonate (**1a**) in prep form, however, does show a notable reduction in total HR, a large increase in char yield, and reductions in peak HRR. This suggests that it is reacted into the polyurethane (further supported by ^{31}P NMR data as well as elemental analysis), as it is soluble in the wash solvent, just as phosphonate **1b** was described above, and if washed out, there would be no signal in the NMR, no %P in the elemental analysis, nor reduction in heat release. What form of the phosphonate is reacted into the polyurethane (through the epoxy groups or through the methyl esters on the phosphorus) is not clear at this time.

Table II. Phosphorus Elemental Analysis Results for the Prep PU Samples, Prepared with the Use of 10 mol % of FR

Compound	Theoretical %P (based on complete incorporation of the FR, 10 mol % used) (%)	Actual %P (ICP analysis) (%)	Estimated actual incorporation of FR (mol %)
DMEP, 1a	0.628	0.610	9.7
ECPH, 1b	0.581	0.210	3.6
DEEP, 2a	0.576	0.572	9.9
ECP, 2b	0.564	0.419	7.4
DECP, 3	0.486	0.391	8.0

All results from ICP atomic emission spectroscopy (GLI procedure ME-70).

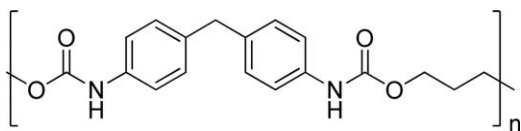


Figure 2. Model polyurethane used for flame retardant screening.

The next group of flame retardants studied was the epoxy phosphates and the heat release reductions measured for these materials in polyurethane are shown in Table IV. Blend samples of phosphonates **2a** and **2b** showed little effect on total HR reduction suggesting that like the epoxy phosphonates, discussed above, these materials do not impart lasting thermal stability to chars that would remain behind at the end of the test and lower total fuel load/polymer combustion. There are some minor increases in char yield noted in the presence of these phosphates in blend form, but otherwise little benefit noted. The epoxy phosphates in blend form, however, do change the HRR curve for the samples, suggesting that they are volatilizing and having some flame retardant effect as the peak HRR values in the Blend samples are reduced (Figure 4). In the Prep samples, the effects of the epoxy phosphates on heat release (total HR and peak HRR) are very structure dependent. The epoxy cyclophosphate **2b** in Prep form imparts high char yields and a notable reduction in total HR, but it increases the peak HRR value significantly (Figure 4). This may suggest that once this phosphate is incorporated into the polyurethane, it forms char late in the combustion of the sample. Specifically the polyurethane still decomposes (and perhaps decomposes faster initially) giving off initial heat release, but then what remains behind is thermally stable and resists further pyrolysis, thus lowering total HR as more of the polymer “fuel” is trapped behind. It can be inferred that phosphate **2b** is incorporated into the polyurethane structure because it is readily soluble in methanol, and so it would have been washed out of

the polymer during Prep synthesis. Further, the signals detected by ^{31}P NMR (Table I) also suggest incorporation, and the elemental analysis (Table II) show that most of the FR did incorporate into the polyurethane as well. This notable difference in performance is even more interesting when compared to the heat release measured from the polyurethane containing epoxy phosphate **2a**, where the cyclic phosphate structure has been replaced with two ethoxy groups. Epoxy phosphate **2a** can also be inferred to have reacted into the polyurethane as it would have washed out (readily soluble in methanol) and we observe changes to the HRR curve (Figure 4) suggesting some sort of reaction. Further, there are again signals in the ^{31}P NMR indicating reaction of this FR into the PU structure and elemental analysis shows a high degree of incorporation in the polyurethane. The nature of the incorporation of phosphate **2b** into the PU, in regards to chemical structure, cannot be inferred as we do not have structural information, but the results from the ^{31}P NMR data suggest that the structure may be changed since multiple peaks are detected.

The remaining phosphate, **3**, is different than the other two epoxy phosphates in that it has two epoxy groups and a pendant carbonate group. This material shows FR effectiveness in both blend and prep forms, with the blend form showing some heat release reduction (Table IV). ^{31}P NMR data (Table I) shows that the FR is reacted into the PU, but due to the complexity of structure, which chemical form is present cannot be determined from the data. Elemental analysis shows that the phosphate did incorporate into the structure at good levels, and for something with lower levels of total active phosphorus, it appears that this FR may have some additional benefit of heat release reduction, due to its structure, that cannot just be explained by %P content. While the data in this article cannot determine the mechanism of flame retardancy exactly, the changes in HRR curve

Table III. Heat Release Data for Epoxy Phosphonates

Sample	Char yield (wt %)	HRR peak (s) value (W/g)	Total HR (kJ/g)	Total HR % reduction (%)
PU Control	8.87	267, 162	21.8	0.0
PU Control	9.22	275, 158	22.2	0.0
PU Control	8.39	207, 144	21.9	0.0
PU Prep with 1a Run 1	24.24	15, 153, 64	17.9	18.5
PU Prep with 1a Run 2	24.58	16, 154, 63	18.0	18.1
PU Prep with 1a Run 3	24.56	16, 156, 65	18.3	16.7
PU Blend with 1a Run 1	12.27	177, 258, 232, 124	24.9	-13.4
PU Blend with 1a Run 2	11.90	139, 310, 213, 121	24.7	-12.4
PU Blend with 1a Run 3	12.09	93, 345, 219, 119	24.3	-10.6
PU Prep with 1b Run 1	11.77	8, 324, 97	21.7	1.2
PU Prep with 1b Run 2	11.58	8, 303, 102	21.8	0.8
PU Prep with 1b Run 3	11.52	8, 295, 107	21.9	0.3
PU Blend with 1b Run 1	13.81	246, 146, 177	26.6	-21.1
PU Blend with 1b Run 2	14.33	188, 140, 187	24.3	-10.6
PU Blend with 1b Run 3	14.12	201, 185	24.4	-11.1
PU Blend with 1b Run 4	14.14	213, 145, 183	25.0	-13.8

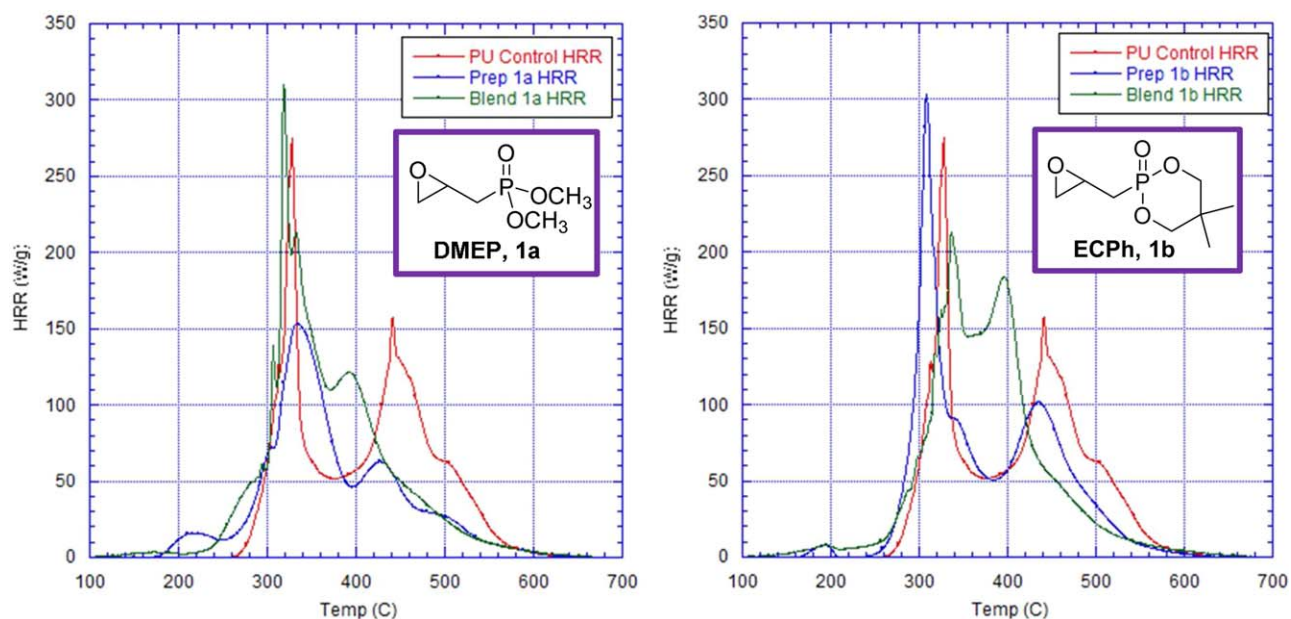


Figure 3. HRR plots for epoxy phosphonates **1a** (left) and **1b** (right). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

shape (Figure 5), as well as enhanced char yield, suggest that there is some condensed phase char formation occurring with this material. Peak HRR values are reduced as well suggesting that this potential FR could reduce flaming intensity once the sample is ignited.

CONCLUSIONS

The results from this article suggest that the use of epoxy groups on phosphonate and phosphate structures does allow for some additional potential of reaction into the polyurethane backbone during polymer synthesis, but the complexity of the

Table IV. Heat Release Data for Epoxy Phosphates

Sample	Char Yield (wt %)	HRR peak (s) Value (W/g)	Total HR (kJ/g)	Total HR % reduction (%)
PU Control	8.87	267, 162	21.8	0.0
PU Control	9.22	275, 158	22.2	0.0
PU Control	8.39	207, 144	21.9	0.0
PU Prep with 2b Run 1	12.49	231, 82, 122	20.5	6.7
PU Prep with 2b Run 2	12.59	188, 83, 134	20.7	5.8
PU Prep with 2b Run 3	12.05	138, 128, 86, 153	21.0	4.4
PU Blend with 2b Run 1	13.56	178, 151, 157, 130	21.6	1.7
PU Blend with 2b Run 2	13.15	171, 152, 133	22.0	-0.2
PU Blend with 2b Run 3	12.64	198, 152, 126	22.1	-0.6
PU Prep with 2a Run 1	16.50	327, 83	19.6	10.8
PU Prep with 2a Run 2	15.60	328, 82	18.4	16.2
PU Prep with 2a Run 3	16.57	328, 87	19.6	10.8
PU Blend with 2a Run 1	12.38	226, 199, 103	24.3	-10.6
PU Blend with 2a Run 2	12.67	237, 200, 103	24.1	-9.7
PU Blend with 2a Run 3	12.70	249, 203, 104	23.7	-7.9
PU Prep with 3 Run 1	12.36	114, 117, 84, 127	20.1	8.5
PU Prep with 3 Run 2	12.40	115, 101, 85, 125	20.2	8.0
PU Prep with 3 Run 3	12.34	124, 117, 81, 130	20.3	7.6
PU Blend with 3 Run 1	13.17	139, 203, 178	20.9	4.9
PU Blend with 3 Run 2	12.30	148, 209, 178	21.0	4.4
PU Blend with 3 Run 3	12.58	135, 225, 173	20.9	4.9

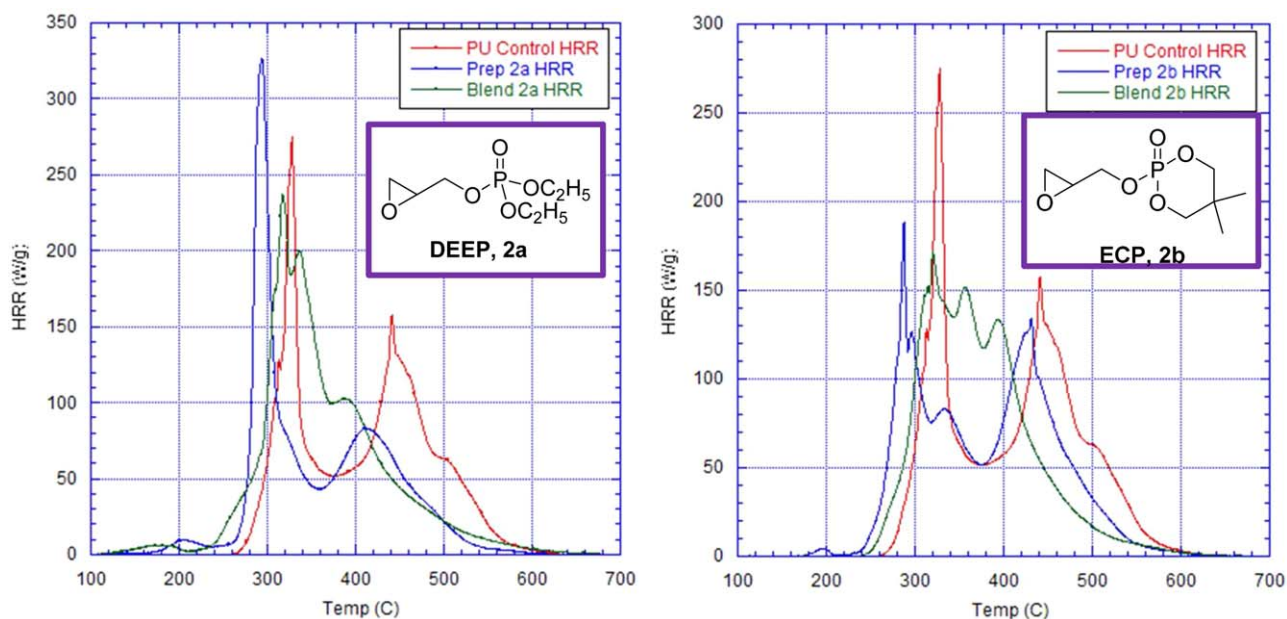


Figure 4. HRR plots for epoxy phosphates 2a (left) and 2b (right). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

^{31}P NMR signal suggests that the reaction may not be as expected, and some of the structures may be changed upon reaction/incorporation into the polymer. Further, the elemental analysis results indicate that some of these potential FRs do have high levels of reactivity with the polyurethane and show high levels of incorporation, namely alkyl phosphorus compounds **1a** and **2a**. The cyclic phosphorus compounds **1b** and **2b** have lower levels of incorporation, but not to the same degrees, and the diepoxy carbonate phosphate **3** also shows good incorporation levels, but not near the theoretical value. In

any event, the incorporation levels are structure dependent and complex, and require additional study.

The ability of these new chemicals to have flame retardant effects was also very structure dependent. The phosphonates, when blended into the PU, had a negative effect on heat release suggesting that they simply volatilized and burned off during heating. When reacted into the PU, the cyclic phosphonate **1b** showed no reduction in heat release while the alkyl phosphonate **1a** did show some effect on heat release reduction. The enhanced char yield and changes in HRR curve shape suggest a condensed phase mechanism for this phosphonate, but more chemical studies would be needed to confirm this. Still, an increased char yield strongly points toward a condensed phase mechanism of flame retardancy. The phosphates **2a** and **2b**, similar to the phosphonates, had little effect in blend form, but did show some char formation and condensed phase flame retardant effect when reacted into the PU. As with the phosphonate data, the complexity of the ^{31}P NMR data after reaction hints that the phosphate chemical structure may have changed when reacted into the PU backbone, but the data does not indicate what that chemical change was. Still, even if change occurred, some flame retardancy potency still exists even after the change. Phosphate **3**, on the other hand, showed itself to have some middling levels of flame retardant potency, but when looking at the %P incorporation, with phosphate **3** having the least amount of phosphorus in its structure, it appears to have a bit more heat release reduction potential per molecule, assuming that phosphorus is the active part of the flame retardant structure. Therefore, other parts of this structure, such as the carbonate, may be having an effect but more definitive analysis is needed to validate this hypothesis.

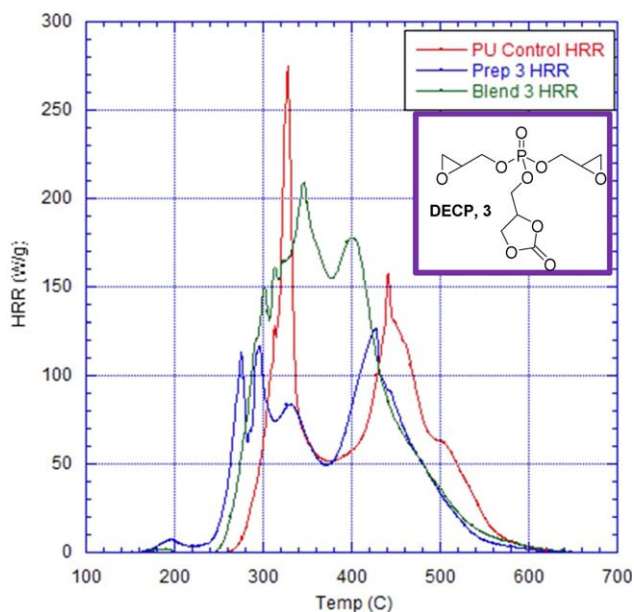


Figure 5. HRR plot for epoxy phosphate 3. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

The results from this study show that development of new reactive flame retardants for polyurethanes is not easy nor is

straight forward. More detailed chemical analysis of resulting polymer + FR structures is needed along with validation that certain levels of heat release reduction are meaningful in regards to regulatory fire tests which require more materials. Still, despite the uncertainty of the practical value of the results in this article, the results show some promise of chemical structures that do incorporate into polyurethane and do show some enhanced char formation and heat release reduction. From this data, further experiments can be done by others to validate the results or show that the potential FRs have other problems and thus can be eliminated as future molecules of study.

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