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LDRD PROJECT TITLE: Organoboron Based Antioxidants

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ABSTRACT

Earth's environment can be considered especially harsh due to the cyclic exposure of heat, moisture, oxygen, and ultraviolet (UV) and visible light. Polymer-derived materials subjected to these conditions over time often exhibit symptoms of degradation and deterioration, ultimately leading to accelerated material failure. To combat this, chemical additives known as antioxidants are often used to delay the onset of weathering and oxidative degradation. Phenol-derived antioxidants have been used for decades due to their excellent performance and stability; unfortunately, concerns regarding their toxicity and leaching susceptibility have driven researchers to identify novel solutions to replace phenolic antioxidants.

Herein, we report on the antioxidant efficacy of organoborons, which have been known to exhibit antioxidant activity in plants and animals. Four different organoboron molecules were formulated into epoxy materials at various concentrations and subsequently cured into thermoset composites. Their antioxidant performance was subsequently analyzed via thermal, colorimetric, and spectroscopic techniques. Generally, thermal degradation and oxidation studies proved inconclusive and ambiguous. However, aging studies performed under thermal and UV-intensive conditions showed moderate to extreme color changes, suggesting poor antioxidant performance of all organoboron additives. Infrared spectroscopic analysis of the UV aged samples showed evidence of severe material oxidation, while the thermally aged samples showed only slight material oxidation. Solvent extraction experiments showed that even moderately high organoboron concentrations show negligible leaching susceptibility, confirming previously reported results. This finding may have benefits in applications where additive leaching may cause degradation to sensitive materials, such as microelectronics and other materials science related areas.

INTRODUCTION AND EXECUTIVE SUMMARY OF RESULTS

The 20th century saw enormous changes in all facets of human life.[1] One aspect of this change occurred in the area of material science, where traditional materials (wood, iron, steel, etc.) were increasingly supplemented with synthetic materials derived from polymers, giving rise to what many social scientists now refer to as "The Plastic Age".[2]

Due to reduced manufacturing costs and improved performance attributes compared to traditional materials, polymeric materials became mainstream and found use in applications ranging from architecture and infrastructure to aerospace and defense materials. These newer materials were stronger, more lightweight, and more durable than traditional materials, however it was soon recognized that outdoor exposure could greatly decrease their service life.[1, 3] Thus, there quickly arose a need for understanding, measuring, and ultimately delaying the degradative effects of the natural environment on polymeric materials.

The combined degradative material effects that result from exposure to Earth’s environment is commonly referred to as “weathering". The weathering process involves a series of complex chemical reactions and is often influenced by the synergistic effects of heat (thermal degradation), light (photodegradation), ionizing radiation (radiolytic degradation), and moisture (hydrolytic degradation).[4-8] Depending on the substrate, symptoms of weathering may take the form of rusting and corrosion (metal) or material embrittlement, cracking, and fracture (polymers and ceramics).

One of the most fundamental chemical reactions leading to weathering is oxidation, which can be defined as a chemical reaction between a material substrate and environmental oxygen. Analogous to the examples above, this mode of failure is often generally categorized under the term “oxidative degradation”, but it often occurs in the presence of other weathering factors, such as heat, light, and moisture. Oxidation may occur via two different routes; in one route, heat and light may cause environmental oxygen to break down into reactive oxygen species (ROS, Figure 2), which can react with the material substrate surface. In another route, heat and light may cause the chemical bonds on the material surface to break down, causing a chain reaction in the presence of oxygen that further deteriorates the material.[9] For polymer-derived materials, the second route has been postulated to occur via the scheme shown in Figure 1, where R represents a generic carbon species (alkyl, aryl, etc.)[10]

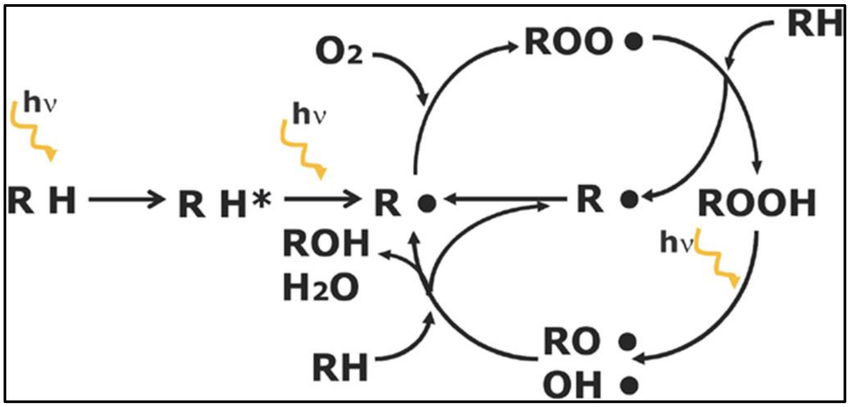


Figure 1. Oxidation mechanism of polymer-based materials, where heat/light may cause the breakdown of chemical bonds on the polymer surface, which may go on to react with environmental oxygen.

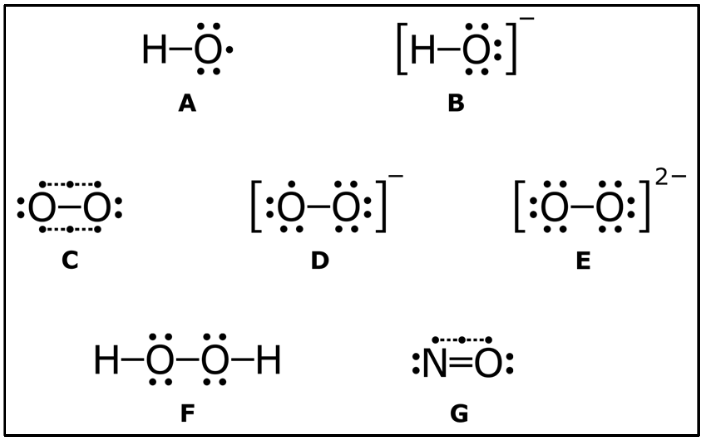


Figure 2. Various ROS molecules that may be generated from environmental oxygen and can participate in oxidation reactions. A. Hydroxyl radical, B. Hydroxide anion, C. Triplet oxygen, D. Superoxide anion, E. Peroxide ion, F. Hydrogen peroxide, G. Nitric oxide (requires nitrogen source).

Polymer-derived materials represent an ever-growing segment in the civil engineering, aerospace, and defense industries. Unlike traditional materials, polymer-derived materials can be designed to withstand a range of exceedingly harsh environments, either through polymer design or formulation with performance enhancing additives. One of the most common types of chemical additives are antioxidants, which neutralize the ROS before polymer degradation can occur. Phenolic chemistries (Figure 3) are the most popular type of antioxidants due to their high reactivity towards ROS and their exceptional long-term stability.[11-13] However, phenolic antioxidants are toxic, slightly corrosive/acidic, and can leach from plastic materials over time. Additionally, they can off-gas corrosive byproducts during the ROS neutralization reaction. In instances where polymer compounds are used to protect highly sensitive equipment (e.g., epoxy encapsulation of microelectronics), leaching and off-gassing can contaminate or otherwise ruin these systems.[14] For these reasons, multiple mission critical areas within Sandia National Laboratories have identified an urgent need to replace phenolics with less problematic compounds.

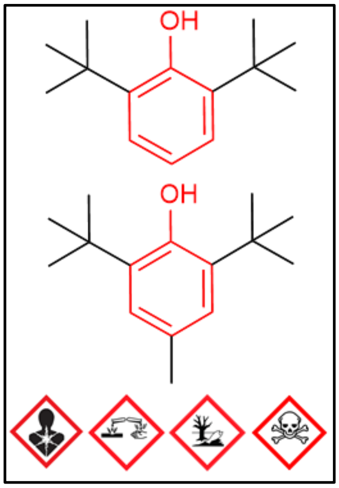


Figure 3. Example of common phenolic molecules used as antioxidant additives, 2,4-di-tert-butylphenol (top) and butylated hydroxytoluene (bottom), alongside their associated health and toxicity warning labels.

Small molecule additives, including antioxidants and others, are often formulated into thermoplastic and thermoset materials destined for use in field applications. With regards to leaching tendency, it may be assumed (incorrectly) that leaching occurs primarily in thermoplastic materials, due to the uncrosslinked nature of these materials.[15] Unfortunately, it has been extensively documented that small molecule additives can also leach out of crosslinked materials.[16, 17] One of the most commonly used crosslinked materials are epoxy based thermosets. Epoxies are used in a variety of applications, ranging from adhesives, encapsulants for sensitive electronic components, and as a matrix material for high-performance composites. They are typically composed of a difunctional epoxy resin and a multifunctional amine-based curing agent, which, upon mixing and curing at elevated temperatures, results in a densely crosslinked structure that exhibits excellent mechanical and chemical stability.

Despite their desirable performance attributes, epoxy materials are well known to undergo extensive oxidation when used in various applications. Surface oxidation may take the form of discoloration and yellowing, surface cracking, increased brittleness, and subtle changes in surface chemistry that may impact future material robustness.[18-20] Continued exposure will exacerbate these issues, inevitably resulting in material breakdown and failure. To extend their field life, phenolic antioxidants are formulated into the epoxy material, due to their excellent antioxidant performance and their high chemical compatibility with the epoxy/crosslinker chemistries.[20-22] However, even in highly crosslinked epoxy systems, phenolic antioxidants have been reported to migrate and leach into the environment over time, especially as the epoxy structure begins to break down from continued oxidative degradation.[23-26]

Previous Climate late-start LDRD work (PI: C. Corbin) focused on synthesizing epoxy-based materials that would take advantage of this leaching phenomenon, in an effort to design novel materials that could be used primarily for enhanced degradation, but could have potential applications as advanced filtration and membrane materials.[27] In this instance, boric acid was incorporated into a variety of epoxy/amine formulations at a variety of concentrations. In some formulations, boric acid dissolved easily into the epoxy crosslinker; in others, a precipitate was formed, yielding an inhomogeneous mixture of liquid crosslinker and solid precipitate. For the liquid mixtures containing boric acid, addition of the epoxy component and subsequent curing yielded boric acid doped epoxy composites. Static and dynamic extraction experiments performed on these materials resulted in very low, almost negligible extractable content, demonstrating that boric acid was likely covalently bound within the epoxy material.

For this project, we sought to investigate various trivalent organoboron molecules (Figure 4) to determine if the presence of aliphatic/aromatic functional groups bound to the borate oxygen would impact their susceptibility towards leaching and extraction. We also sought to investigate the antioxidant properties of these organoboron molecules, as organoboron species have been reported to display antioxidant activity towards ROS due to the inherently electron deficient atomic structure of boron.[28] The antioxidant mechanism of boron molecules has also been shown to be similar to phenolic antioxidants, without the off-gassing of corrosive byproducts. Furthermore, there have been a number of studies demonstrating the antioxidant activity of boron *in vivo*, but the efficacy of boron as an antioxidant in materials has received little interest and is currently poorly understood.[29, 30]

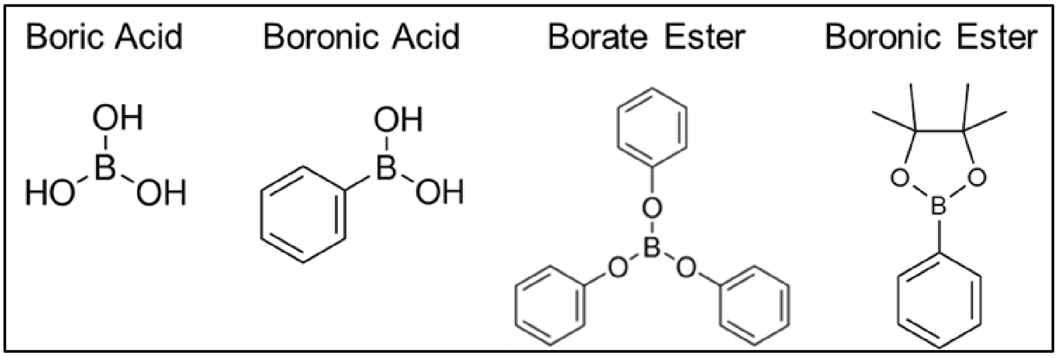


Figure 4. Organoboron compounds used in this study.

DETAILED DESCRIPTION OF RESEARCH AND DEVELOPMENT AND METHODOLOGY

1. Materials

Boric acid (BA, >99.5%), diethanolamine (DEA, puriss, >99.0%, ACS Reagent grade), phenylboronic acid (PBA, 95%), phenylboronic acid pinacol ester (PAPE, 97%), and triphenyl borate (TPB, ≥97%), were purchased from Sigma-Aldrich and used as received. Deuterated chloroform ($CDCl_3$) were purchased from Sigma-Aldrich and used as received. Epon 828 resin was purchased from Hexion and used as received. Deionized water (DI Water) was produced in house.

2. Characterization

2.1. Nuclear Magnetic Resonance (NMR)

NMR measurements were performed using a 500 MHz Bruker AVANCE III NMR (TopSpin 3.6) spectrometer. All ^1H chemical shifts were referenced to the residual solvent peak (7.26 ppm for $CDCl_3$) or TMS. Samples were prepared by dissolving the material in $CDCl_3$ (5%, w/v) and charging this solution to a 7 mm NMR tube.

2.2. Fourier Transform Infrared Spectroscopy (FTIR)

FTIR analysis was performed using a ThermoFisher Nicolet iS20 FTIR Spectrometer equipped with a Smart iTX Diamond Attenuated Total Reflectance (ATR) accessory and a KBr beam splitter. Spectra were obtained in the range between 650-4,000 cm^{-1} with an average of 32 scans at 0.482 cm^{-1} resolution.

2.3. Oxidation Induction Time (OIT)

OIT measurements were performed using a TA Instruments Q-2000 DSC. Approximately 10.0-15.0 mg of cured sample was transferred into an uncovered aluminum pan and heated to 230 °C (heating rate = 20 °C/min) under nitrogen (N_2, flow rate 50 ml/min). After holding isothermally at 230 °C for 5 minutes, the furnace gas was subsequently switched to dry air (flow rate 50 ml/min). For data analysis, the switch from N_2 to air was designated T_0 and used as the start time for the OIT test. The samples were then isothermed in air at 230 °C for 100 minutes, or until the onset of oxidative degradation, which is usually indicated by a sharp increase in exothermic heat flow.

2.4. Thermogravimetric Analysis (TGA)

TGA experiments were performed using a TA Instruments Q5500 TGA, equipped with an IR heater. Runs were performed under dry N_2 with a flow rate of 25 mL/min or dry compressed air with a flow rate of 16 ml/min. Samples were heated from 27 to 600 °C using a heating ramp rate of 5 °C/min.

2.5. Colorimetric Analysis

Colorimetric analysis was performed using an X-Rite CI60 Handheld Color Spectrophotometer programmed and calibrated in the L*a*b* color space. Prior to taking measurements, the spectrophotometer was calibrated using white and black backgrounds. Epoxy samples, which were clear and translucent, were placed against a paper-white background to achieve uniform color measurements. An average of 3 color measurements per sample were made, and Delta E values were calculated after the conclusion of the prescribed aging treatment.

Preparation of Organoboron-Epoxy Mixtures

Organoboron-epoxy mixtures were prepared using four different mole percent concentrations (1.0, 2.5, 5.0, and 10.0 mol%) of the specific organoboron via the following procedure, which is representative.

To a dry 200 mL glass jar containing a magnetic stirbar were charged 1.4984 g of PBA and 70.0891 g of Epon 828. The jar was then moved to a hotplate, loosely covered with aluminum foil, and the mixture was equilibrated to 70.0 °C with vigorous stirring. The mixture was stirred at temperature for 2-4 hours, during which the solid PBA was observed to slowly dissolve over time. After complete dissolution of the phenylboronic acid, the jar was removed from heat and cooled to room temperature. For the TPB formulations, a small amount (~2 mL) of acetone was added to facilitate dissolution of the TPB into Epon 828. After mixing, the residual acetone was removed under vacuum.

For the formulations containing BA, DEA was used as the solvating medium. Thus, 0.9346 g of BA and 10.0068 g of DEA were charged to a scintillation vial equipped with a magnetic stirbar. All subsequent steps were performed as described above.

Preparation of Epoxy Samples

Epoxy composites were prepared using the following procedure, which is representative. To the organoboron/epoxy mixture, a stoichiometric amount of DEA (10.00 g) was added to the jar. The mixture was then stirred vigorously for 2 minutes by hand, and the opaque mixture was then poured into 3-4 disposable aluminum pans. These samples were then placed in an oven (Memmert UF-110 Plus) set to 70 °C and cured for 18 hours. After curing, the aluminum pan was removed and discarded, and the sample was stored for further analysis.

For the boric acid samples, a stoichiometric amount of Epon 828 (70.00 g) was transferred into the boric acid/DEA mixture. All subsequent steps were performed as described above,

Dynamic Solvent Extraction of Cured Epoxy Samples

To determine the susceptibility of organoboron additives towards leaching, dynamic solvent extraction experiments were performed via Soxhlet extraction. Cured epoxy samples were broken into fragments and transferred into tared glass fiber thimbles and weighed prior to the extraction process. Soxhlet extractions were performed under refluxing H_2O for 72 hours, after which the extraction solvent was removed and concentrated via rotary evaporation. In all cases, there was no residual material observed in the roundbottom flask to undergo further characterization. The epoxy samples were dried under vacuum at 70 °C, removed from the glass fiber thimble, then weighed to determine mass loss.

Aging of Cured Epoxy Samples

Two types of material aging were performed for this study. Thermal aging was performed over 1,500 h in a Memmert UF-110 Plus oven set to 70 °C. Samples were removed every 500 h and characterized via FTIR spectroscopy. Color measurements were performed at 0 h aging and after 1,500 h aging.

Ultraviolet (UV) aging was performed using a Suntest XLS+ equipped with a 1,700 W Xenon lamp. Aging was performed over 500 h, with the aging protocol set to 50 minutes of light exposure, followed by a 10-minute dark cycle. FTIR spectroscopy and color measurements were performed at 0 h aging and 500 h aging.

RESULTS & DISCUSSION

Synthesis and Characterization of Liquid Boric Acid-Amine Mixtures

1. Synthesis of Organoboron/Epoxy Mixtures

Organoboron formulations were prepared under neat conditions using either DEA or Epon 828 as the reaction medium. Four formulations for each organoboron were prepared, with the organoboron content ranging from 1.0 – 10.0 mol percent of the formulation. Actual masses of the organoboron used to prepare each formulation are tabulated in Table 1. From the mass of the organoboron used, the appropriate molar amount of Epon 828 (for PBA, PAPE, and TPB formulations) or DEA (for BA formulations) was calculated and subsequently added. For all formulations, this was generally around 70.0 g Epon 828 and 10.0 g DEA. Generally, preparation of the Epon 828 mixtures (i.e., Epon 828/TPB, Epon 828/PBA, and Epon 828/PAPE) and BA/DEA mixtures proceeded smoothly. Elevated temperatures (70 °C) were required to facilitate complete dissolution of the organoboron in a convenient time frame. For the PAPE formulations, complete dissolution occurred within 5-10 minutes, likely facilitated by the low melting point of PAPE (27-30 °C). For the PBA formulations, complete dissolution took considerably longer, around 2-4 hours. Unlike the PAPE and PBA mixtures, addition of TPB into Epon 828 resulted in slightly hazy mixture (Figure 5). Using 1-2 ml of acetone to dissolve TPB before addition into Epon 828, followed by subsequent removal of acetone via vacuum, resulted in a clear, homogenous mixtures for 1.0-5.0 mol%. Despite repeated efforts, the 10 mol% formulation consistently resulted in a lumpy, gelatinous mixture; thus, it was removed from all subsequent testing. For the BA formulations, complete dissolution in DEA proceeded relatively quickly (~ 30 minutes).

Table 1. Mass of each organoboron constituent used in each formulation, alongside associated mol fraction.

	1.0 mol% (g)	2.5 mol% (g)	5.0 mol% (g)	10 mol% (g)
BA	0.1784	0.4531	0.9346	1.9600
PBA	0.3760	0.8330	1.7984	4.6953
PAPE	0.5619	1.3359	3.0779	6.5383
TPB	0.8210	2.0820	3.5570	-

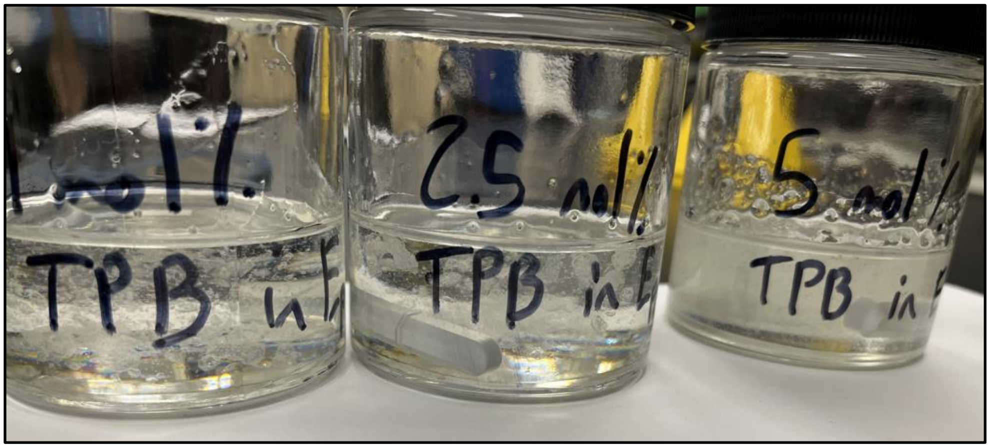


Figure 5. Hazy mixtures resulting from addition of TPB into Epon 828.

At ambient temperature, all formulations remained clear and mostly colorless. The only exception was the PBA formulation, which took on a slight yellow color at higher PBA concentrations (shown in Figure 6). Also, the dynamic viscosities of each mixture were significantly higher than pure Epon 828 (or in the case of BA, pure DEA), but samples could still be poured and hand-mixed without issue.

Characterization of Organoboron Mixtures

To better understand the chemical nature of the organoboron mixtures, the liquid mixtures were characterized via NMR (^{1}H) and FTIR prior to curing into epoxy composites.

2.1 Characterization via NMR

The liquid mixtures of all systems were characterized via ^{1}H and their spectra are shown below in Figure 7 through Figure 10. For the BA mixtures shown in Figure 7, the simple structure of DEA resulted in clean, easy to interpret spectra. Comparing the starting material and the liquid reaction product in each formulation shows minimal differences in spectra. The very slight upfield shift of the triplets at 3.65 ppm and 2.72 ppm (shifting to 3.60 and 2.70 ppm respectively) indicate that these protons experience a very minor change in chemical environment. In our previous report, characterization of this precursor material yielded results that suggest that a cyclic borate molecule is being formed *in-situ*.[27]

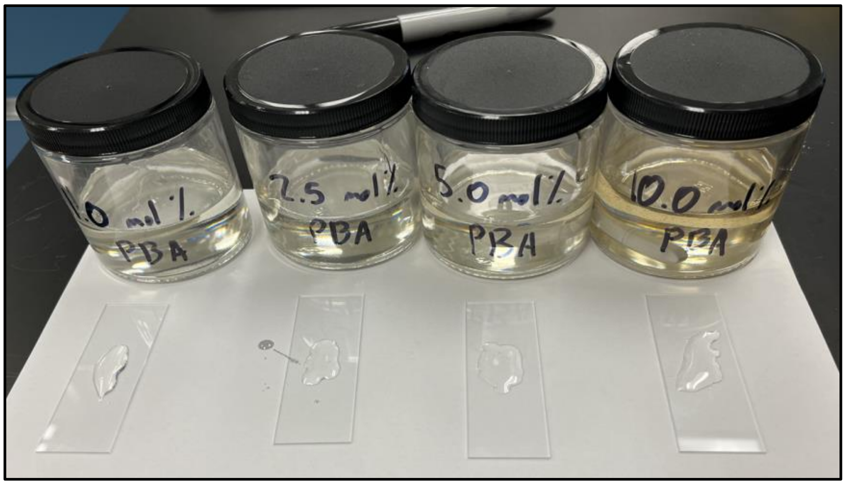


Figure 6. All formulations were clear and colorless, with the exception of the PBA formulations, which took on a slight yellow color as the PBA concentration increased.

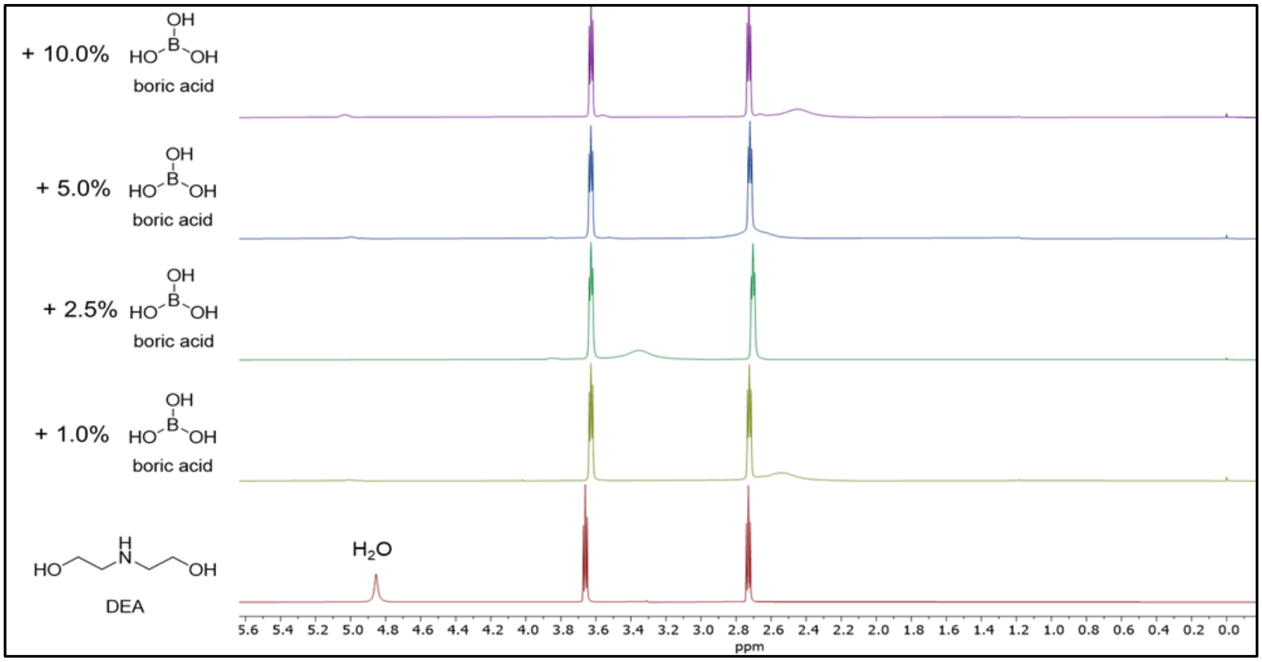


Figure 7. ^1H NMR spectra (500 MHz, $CDCl_3$, 25 °C) of DEA (bottom) and the liquid reaction products of 1.0-10.0 mol% BA.

For the PAPE mixtures shown in Figure 8, tracking the peaks associated with the starting material (Epon 828, bottom spectrum) demonstrates that the peaks do not shift as PAPE is added into the system. This indicates that protons within Epon 828 are not experiencing a change in chemical environment, thus it is unlikely a chemical reaction is occurring. As higher amounts of PAPE are added into the mixture, the peak associated with the methyl protons of the pinacol ester (1.34 ppm) increases in intensity. The lack of splitting pattern of this peak further indicates that the pinacol ester group remains intact throughout the mixing process, reinforcing the hypothesis that no chemical reaction is occurring between PAPE and Epon 828. Also, as the concentration of PAPE increases in the mixture, the peaks associated with the PAPE aromatic protons (7.35-7.85 ppm) begin to increase in intensity.

For the PBA mixtures shown in Figure 9, a similar observation regarding the peaks associated with the starting material (Epon 828, bottom spectrum) can be made. As the concentration of PBA increases, no shift or change in splitting pattern is observed. As higher amounts of PBA are added into the mixture, a singlet belonging to the alcohol protons of PBA increased in intensity. Similar to the PAPE mixtures, the peaks associated with the PBA aromatic protons (7.35-7.85 ppm) increase in intensity as the PBA concentration increases.

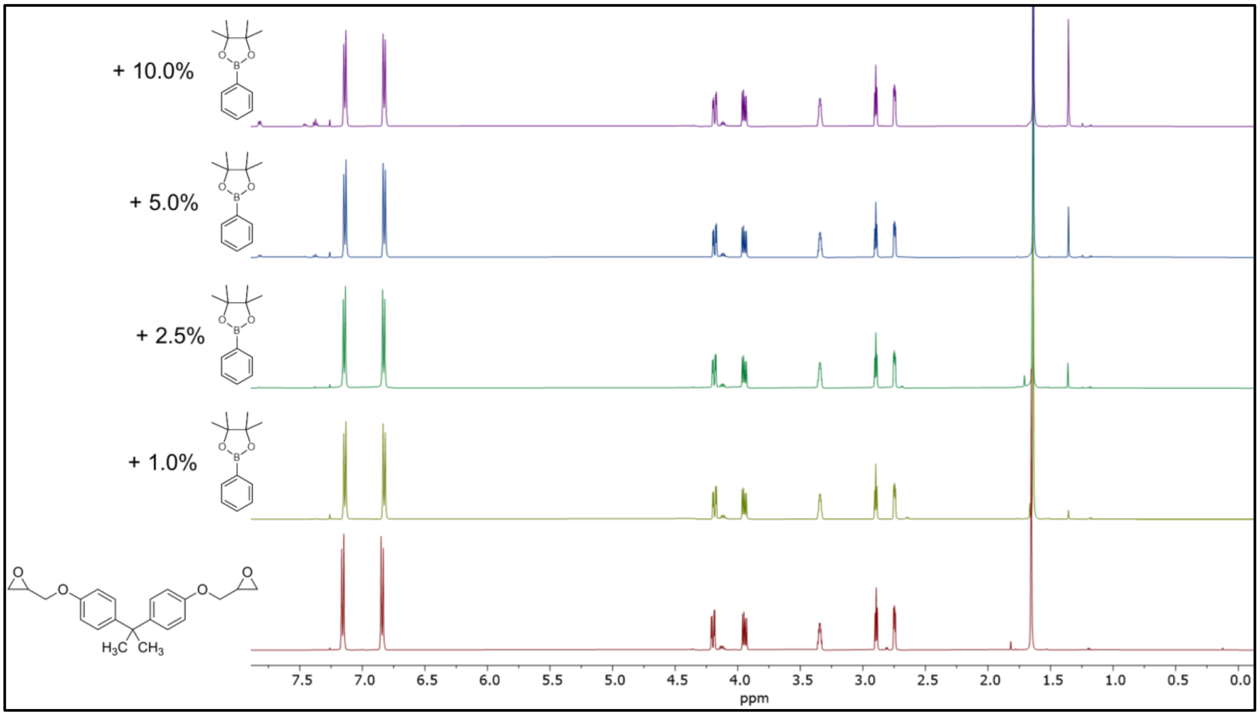


Figure 8. ^1H NMR spectra (500 MHz, $CDCl_3$, 25 °C) of Epon 828 (bottom) and the liquid reaction products of 1.0-10.0 mol% PAPE.

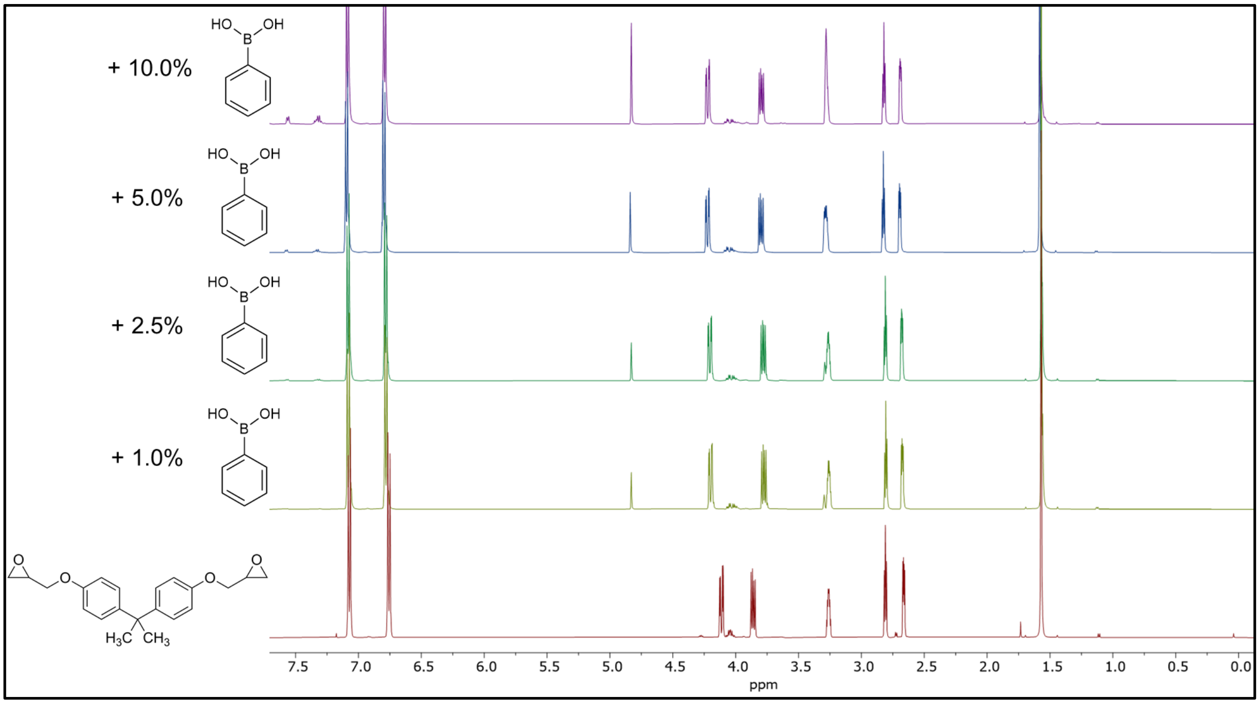


Figure 9. ^{1}H NMR spectra (500 MHz, $CDCl_3$, 25 °C) of Epon 828 (bottom) and the liquid reaction products of 1.0-10.0 mol% PBA.

For the TPB mixtures shown in Figure 10, a similar observation regarding the peaks associated with the starting material (Epon 828, bottom spectrum) can be made. As the concentration of TPB increases, no shift or change in splitting pattern is observed, once again indicating that no reaction between the organoboron and Epon 828 is occurring. As higher amounts of TPB are added into the mixture, the peaks associated with the TPB aromatic protons (6.83-7.14 ppm) begin to overlap with the Epon 828 aromatic proton peaks, resulting in lower peak resolution. As stated above, a small amount of acetone was required to fully disperse the TPB in the Epon 828; despite repeated attempts to remove acetone via high vacuum, a residual acetone peak can be observed at 2.17 ppm. As stated above, the 10.0 mol% TPB mixture was not characterized due to forming an inhomogeneous, gelatinous mixture.

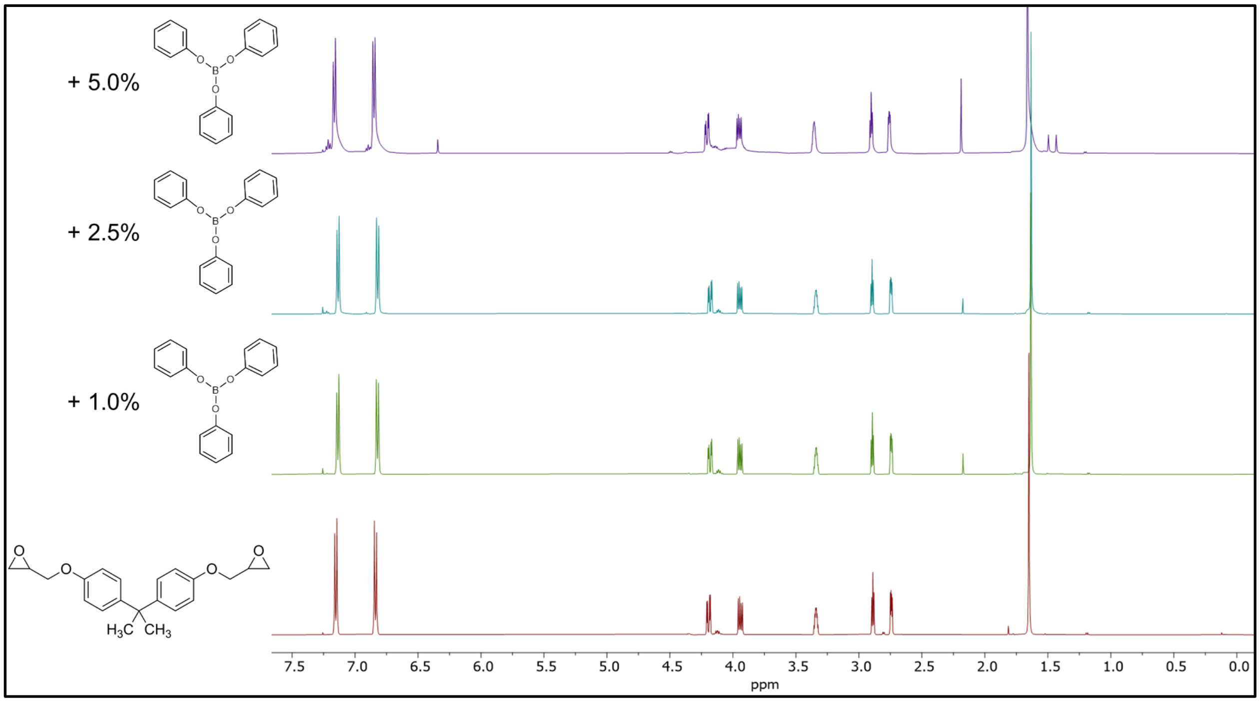


Figure 10. ^{1}H NMR spectra (500 MHz, $CDCl_3$, 25 °C) of Epon 828 (bottom) and the liquid reaction products of 1.0-5.0 mol% TPB.

2.2 Characterization via FTIR

In combination with ^{1}H NMR, chemical analysis of the liquid mixtures was performed using FTIR, which are shown below in Figure 11. Upon close inspection of each FTIR plot, analysis of each liquid mixture was hampered by poor peak resolution and the propensity for boron bond frequencies to fall within the fingerprint region (<1,500 cm^{-1}).[31-35] Significantly, in the case of DEA, the presence of systematic increases in BA concentrations resulted in increased intensity in frequencies associated with B-O stretching (1,330-1,350 cm^{-1}).[36] As expected, the presence of a broad peak within the region typically associated with O-H stretching (3,200- 3,600 cm^{-1}) is observed; however, the peak intensity increases only slightly for formulations containing higher concentrations of BA.[32] This disproportionate change in peak intensity (i.e. significant increase in and B-O stretching peak intensity and slight increase in O-H stretching intensity), gives further evidence towards the existence of covalent B-O species, rather than Lewis acid-base species.

For the remaining mixtures, the incorporation of the organoboron additives resulted in only minor changes within the FTIR spectrum of the Epon 828 starting material. Interestingly, for PBA mixtures, the incorporation of higher loadings of PBA resulted in only a slight increase in the O-H stretching peak. For the TPB system, a small carbonyl peak is observed at ~1,700 cm^{-1}, which is indicative of residual acetone in the mixture.

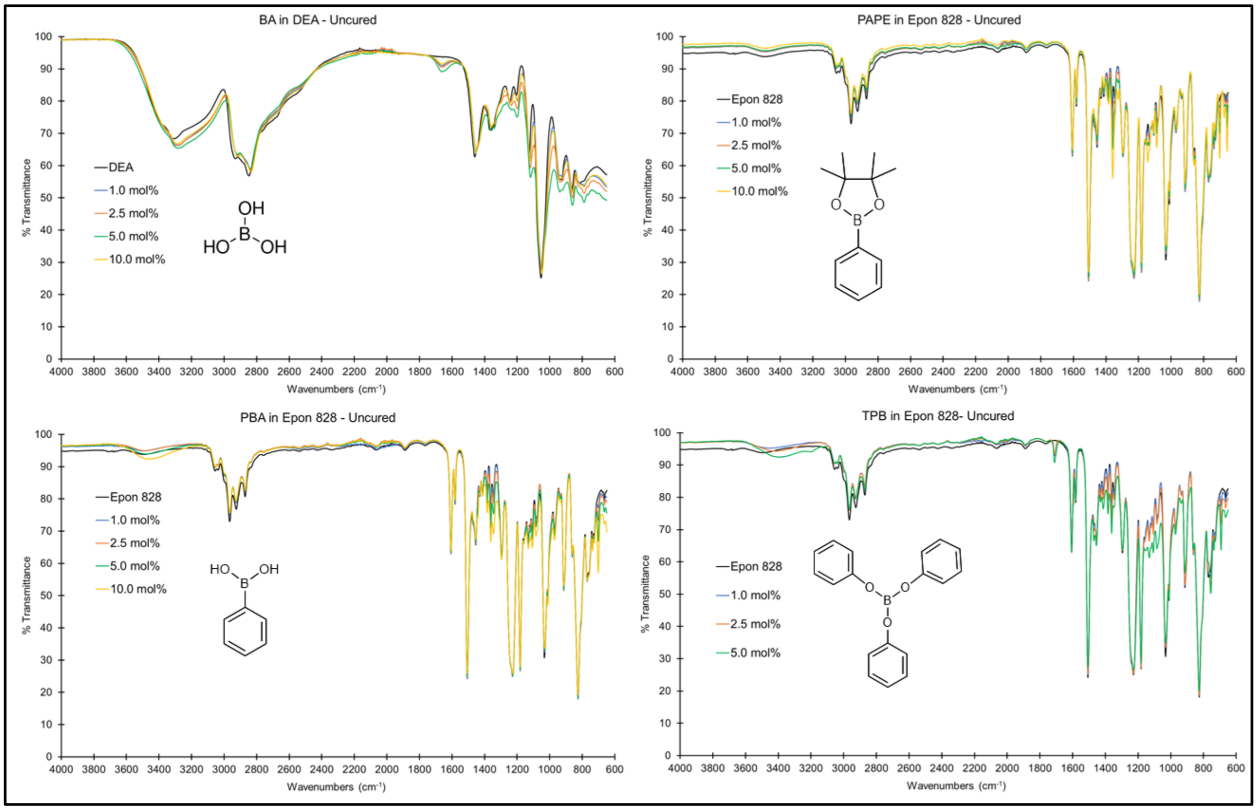


Figure 11. Clockwise from top left, FTIR chromatograms of: DEA/BA liquid mixtures, Epon 828/PAPE liquid mixtures, Epon 828/TPB liquid mixtures, and Epon 828/PBA liquid mixtures.

3. Epoxy Composites- Curing Behavior and Thermal Properties

Epoxy curing studies proceeded smoothly in all but one case, which will be discussed in further detail below. For the PAPE, PBA, and TPB mixtures, DEA (~10.0 g) was added directly into the organoboron/epoxy mixtures at room temperature, followed by vigorous hand mixing and pouring into a disposable aluminum mold. For the DEA/BA formulations, the mixtures were warmed to 70 °C and poured directly into jars containing Epon 828 (~70.0 g). These were subsequently hand mixed and poured into the molds. All samples were cured for 18 hours at 70 °C. The resulting cured epoxy samples are shown below in Figure 12, with all samples being optically transparent and defect free.

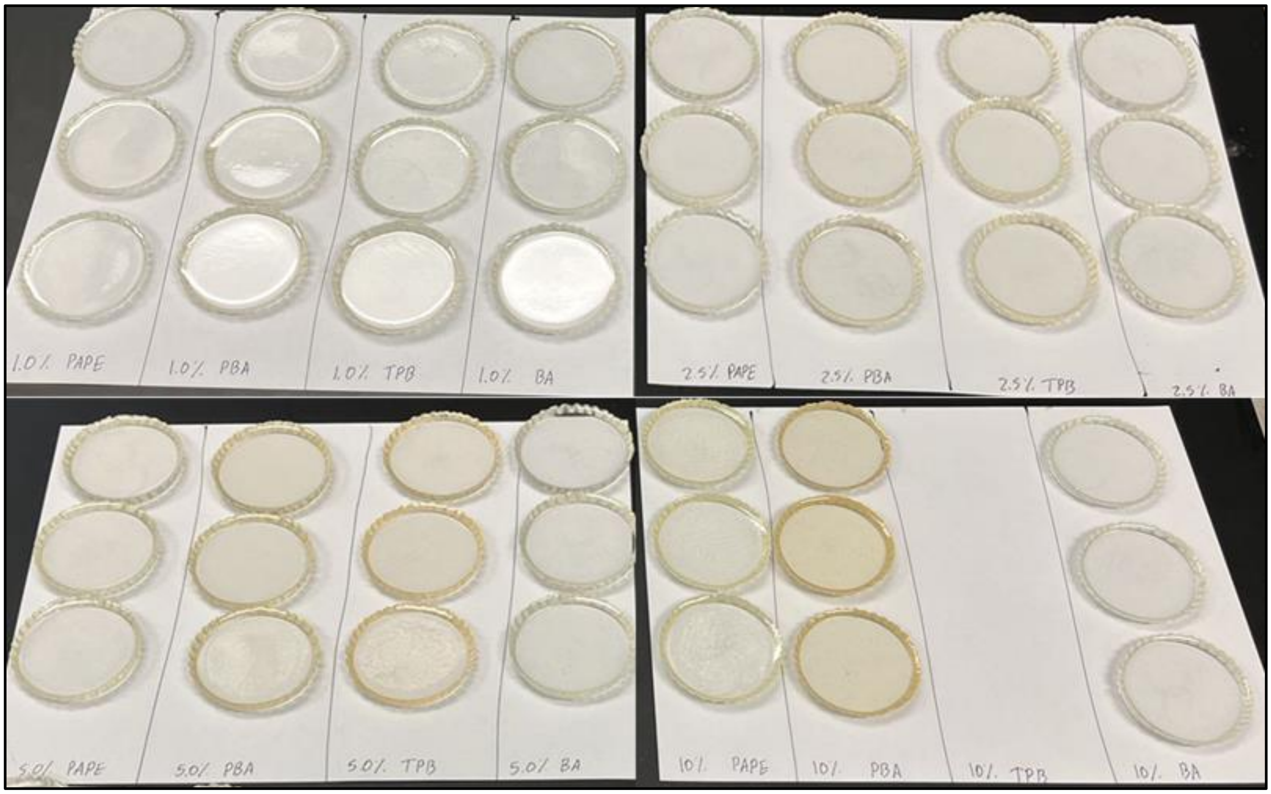


Figure 12. Cured epoxy composite samples of all organoboron formulations, except for the 10 mol% TPB. Epoxy samples were cured at 70 °C for 18 hours.

For the 10 mol% TPB formulation, formation of epoxy composite samples was attempted. It was theorized that the addition of DEA and the elevated curing temperature may help to dissolve the TPB aggregates that were suspended in the liquid mixture. As shown in Figure 13, the resulting composite material shows visually apparent solid aggregates throughout the sample. The sample surface also contained a sticky residue, likely residual uncured Epon 828 or DEA. For these reasons, this formulation was excluded from further testing.

Figure 13. Cured epoxy composite samples of the 10 mol% TPB formulation, showing visible additive aggregation and sample defects. Epoxy samples were cured at 70 °C for 18 hours.

3.1 Epoxy Composites - Thermal Characterization

Thermal degradation behavior of each epoxy composite was probed via thermogravimetric analysis. Experiments were performed in an inert atmosphere (N_2) and in air, which would allow for thermo-oxidative degradation to occur. An overlay of TGA curves for each formulation are shown in Figure 14 (N_2) Figure 15 (air). Data for the temperatures associated with T_{10}, T_{50}, and T_{90} (representing 10% weight loss, 50% weight loss, and 90% weight loss, respectively) are tabulated in
Table 2 through Table 10.

As expected, performing the TGA in an inert atmosphere resulted in a much more uniform weight loss curve, due to the absence of side reactions brought on by oxidative degradation. All samples generally reached 10% weight loss at ~ 350 °C, with the 10 mol% PAPE formulation being the only notable exception at ~304 °C. All formulations generally reached the 50% mass loss threshold (T_{50}) at between 380-390 °C but began to separate as they approached the T_{90} point.

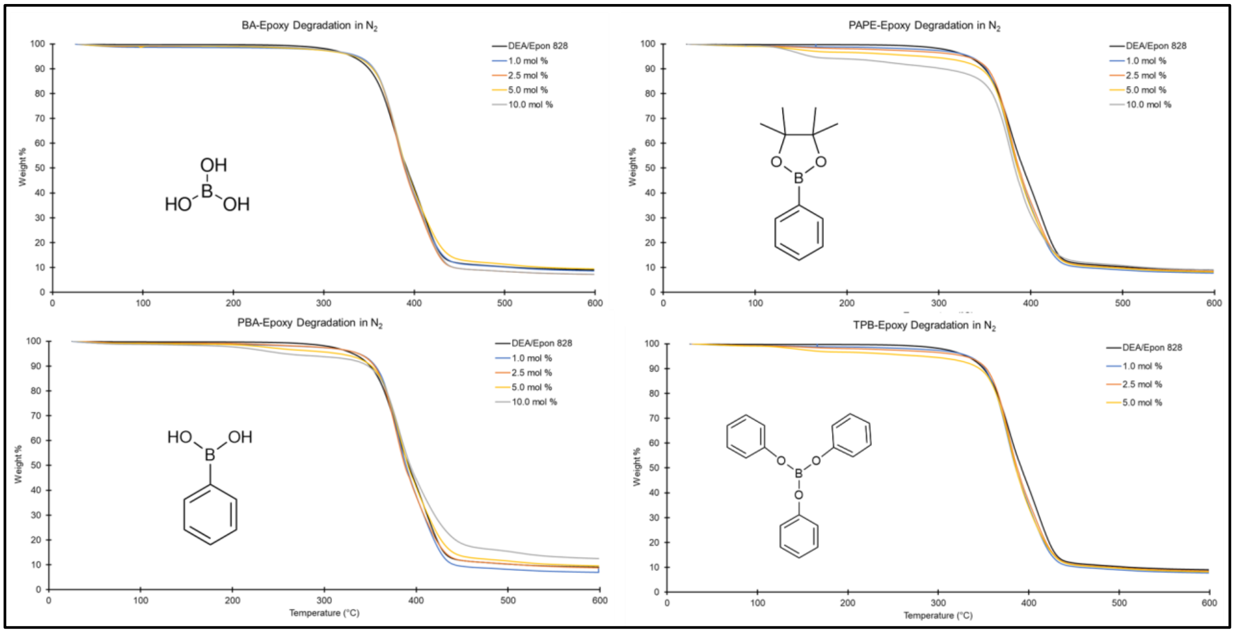


Figure 14. Clockwise from top left, TGA plots of DEA/Epoxy composites containing BA, PAPE, TPB, and PBA additives ranging from 0-10.0 mol%. TGA measurements were performed from 27-600 °C in N_2.

Table 2. TGA (inert) data for epoxy composites containing TPB.

	0.0 mol%	1.0 mol%	2.5 mol%	5.0 mol%
T_{10} (°C)	300.46	293.54	290.03	294.46
T_{50} (°C)	399.43	395.17	397.21	390.39
T_{90} (°C)	557.86	553.82	569.25	555.70

Table 3. TGA (inert) data for epoxy composites containing BA.

	0.0 mol%	1.0 mol%	2.5 mol%	5.0 mol%	10 mol%
T_{10} (°C)	349.93	355.49	354.42	354.07	355.22
T_{50} (°C)	391.81	389.68	389.08	391.08	390.67
T_{90} (°C)	511.99	505.7	443.58	547.40	444.24

Table 4. TGA (inert) data for epoxy composites containing PAPE.

	0.0 mol%	1.0 mol%	2.5 mol%	5.0 mol%	10 mol%
T_{10} (°C)	349.93	351.40	353.03	345.51	304.11
T_{50} (°C)	391.81	385.44	387.10	385.62	382.57
T_{90} (°C)	511.99	457.82	492.85	484.62	525.79

Table 5. TGA (inert) data for epoxy composites containing PBA.

	0.0 mol%	1.0 mol%	2.5 mol%	5.0 mol%	10 mol%
T_{10} (°C)	349.93	355.62	354.63	351.21	347.66
T_{50} (°C)	391.81	388.89	387.47	391.03	393.53
T_{90} (°C)	511.99	441.72	512.3	558.44	-

Table 6. TGA (inert) data for epoxy composites containing TPB.

	0.0 mol%	1.0 mol%	2.5 mol%	5.0 mol%
T_{10} (°C)	349.93	357.15	356.08	351.47
T_{50} (°C)	391.81	390.68	390.86	393.77
T_{90} (°C)	511.99	459.04	449.60	557.30

In general, polymer materials display a higher resistance to thermal degradation while in inert atmospheres but are susceptible to thermo-oxidative degradation in the presence of pure oxygen or air. The TGA plots shown in Figure 15 correspond to analyses that were performed in an aerobic atmosphere, and the change in the degradation profiles of the epoxy composites is readily apparent. Generally, T_{10} occurs much lower at around the ~300 °C mark, with the 10 mol% PAPE material again appearing to be much more susceptible to thermal degradation (T_{10} = 273.36 °C). Interestingly, the thermal degradation profiles of all composites show two distinct regions of degradation, rather than the uniform degradation curves observed in Figure 15. The transition period between regions seems to occur at around 400 °C, which also corresponds to the T_{50} for all formulations. All samples reached their T_{90} point at higher temperatures than their inert counterparts, with some formulations reaching T_{90} at over 100 °C higher than those tested in N_2.

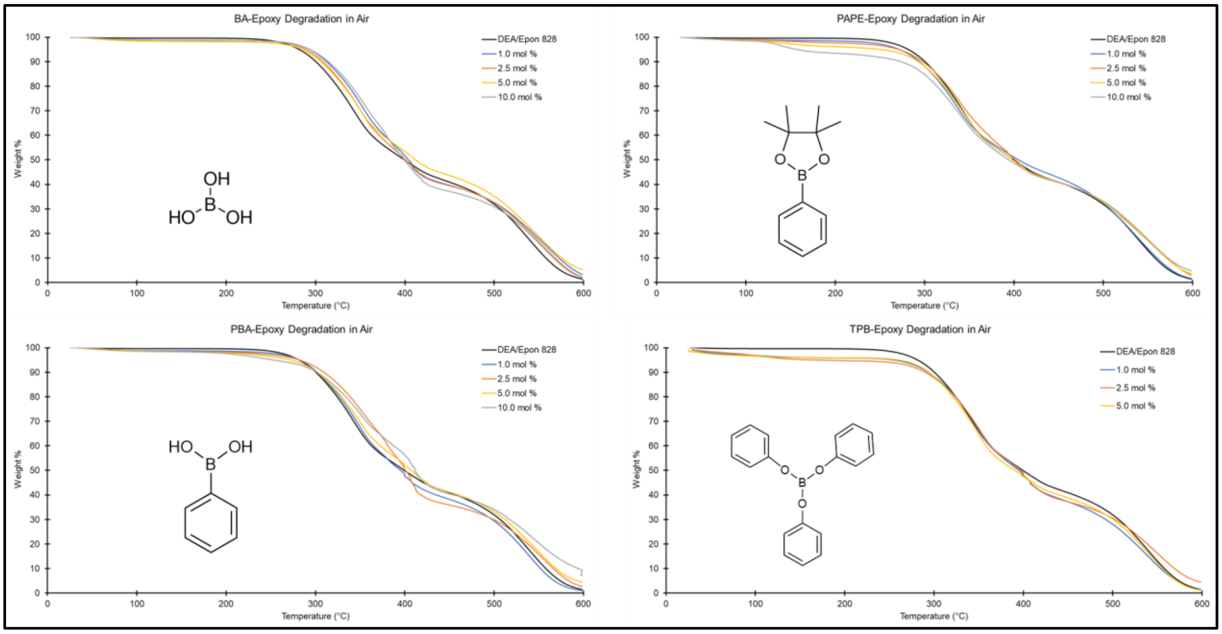


Figure 15. Clockwise from top left, TGA plots of DEA/Epoxy composites containing BA, PAPE, TPB, and PBA additives ranging from 0-10.0 mol%. TGA measurements were performed from 27-600 °C in air.

Table 7. TGA (air) data for epoxy composites containing BA.

	0.0 mol%	1.0 mol%	2.5 mol%	5.0 mol%	10 mol%
T_{10} (°C)	300.46	312.45	308.37	306.05	314.31
T_{50} (°C)	399.43	403.82	400.93	411.86	399.26
T_{90} (°C)	557.86	572.55	568.12	575.58	566.25

Table 8. TGA (air) data for epoxy composites containing PAPE.

	0.0 mol%	1.0 mol%	2.5 mol%	5.0 mol%	10 mol%
T_{10} (°C)	300.46	294.34	298.24	293.07	273.36
T_{50} (°C)	399.43	405.10	401.29	398.24	394.31
T_{90} (°C)	557.86	560.18	571.14	570.56	572.28

Table 9. TGA (air) data for epoxy composites containing PBA.

	0.0 mol%	1.0 mol%	2.5 mol%	5.0 mol%	10 mol%
T_{10} (°C)	300.46	302.02	309.43	301.59	301.44
T_{50} (°C)	399.43	395.28	400.73	407.03	411.58
T_{90} (°C)	557.86	551.97	566.39	569.26	594.13

Table 10. TGA (air) data for epoxy composites containing TPB.

	0.0 mol%	1.0 mol%	2.5 mol%	5.0 mol%
T_{10} (°C)	300.46	293.54	290.03	294.46
T_{50} (°C)	399.43	395.17	397.21	390.39
T_{90} (°C)	557.86	553.82	569.25	555.70

To measure the antioxidant performance of each epoxy composite more directly, OIT testing was performed following the general procedure outlined in Figure 16.[37] Generally, OIT testing involves heating cured epoxy samples 230 °C under nitrogen, after which the furnace gas is switched to air and the test begins. As evidenced in Figure 17, none of the samples tested followed the expected behavior of oxidation onset. Instead, samples displayed relatively stable OIT values until the test was ended at 120 minutes, yielding inconclusive results. One explanation for this behavior may be due to the fact that these samples were thermoset materials; in the literature, OIT testing is often performed on thermoplastic materials in the melt state. In that instance, oxygen diffusion can occur throughout the polymer melt, causing faster degradation. For thermoset materials, only the outer surface of the polymer material comes into contact with air, resulting in a much lower rate of oxidation.

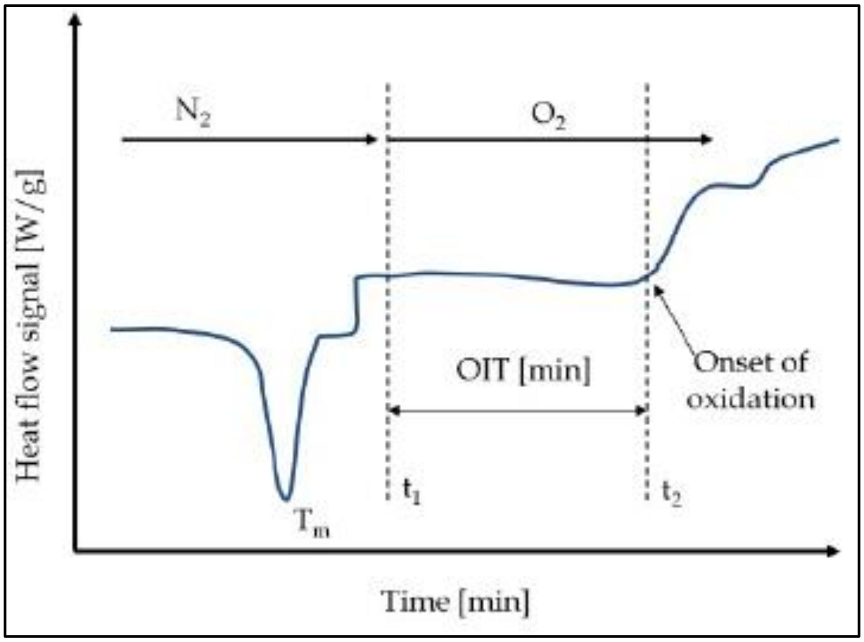


Figure 16. Principle sequence of OIT time measurements according to ISO 11357-6 (2002). Adapted from reference.

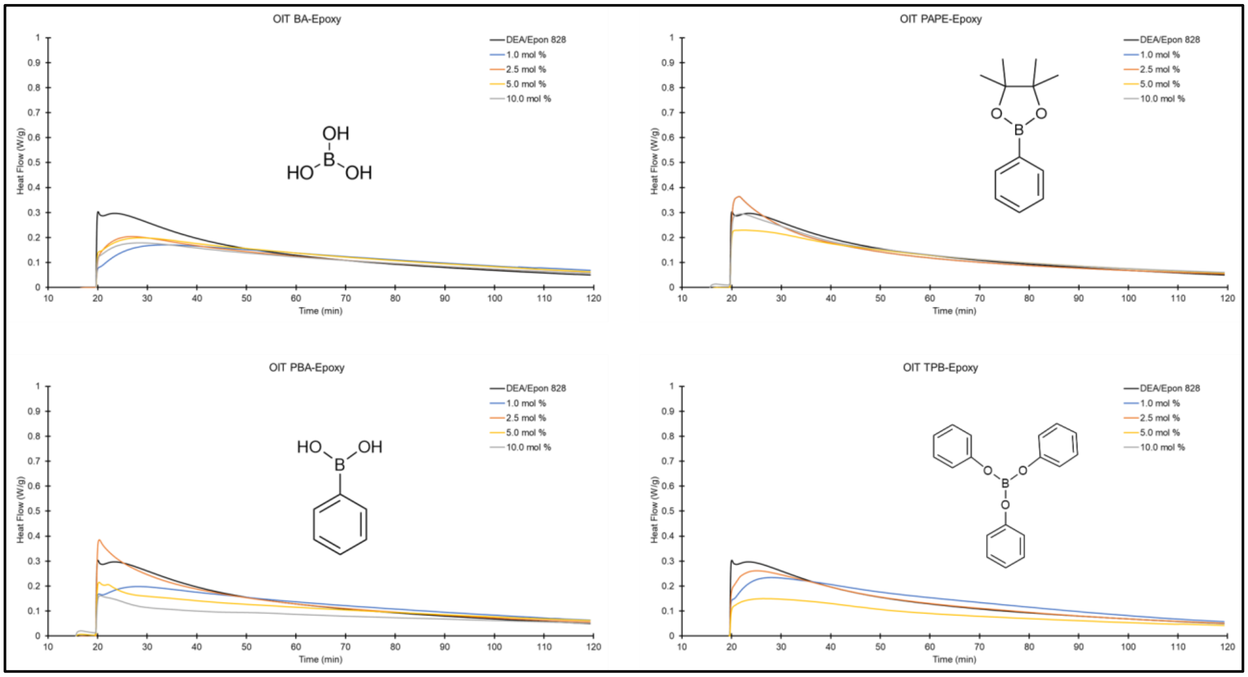


Figure 17. Clockwise from top left, OIT plots of DEA/Epoxy composites containing BA, PAPE, TPB, and PBA additives ranging from 0-10.0 mol%. OIT measurements were taken at 230 °C in an air environment.

3.2 Epoxy Composites- Extraction Experiments

Dynamic solvent extraction experiments were performed on select formulations via Soxhlet extraction, using small fragments of the epoxy composite samples. Small fragments were used in order to increase the surface area contact with the refluxing solvent. Soxhlet extractions were performed over a 72-hour period, using water as the extraction solvent, with each epoxy sample contained 5 mol% organoboron additives. The results of these experiments are shown in Table 11, which show almost negligible leaching results in all formulations tested. These results are similar to systems previously tested with boric acid, which showed extremely low leaching susceptibility when formulated with a variety of epoxy crosslinkers.[27]

3.3 Epoxy Composites- Accelerated Aging Experiments

Accelerated aging of polymer materials is often performed to understand how polymer materials will withstand weathering, without having to wait for prohibitively long timeframes.[38] Two types of accelerated aging were performed on cured epoxy composites, in order to probe the antioxidant performance under thermal and ultraviolet conditions. Samples were aged under thermal conditions for 1,500 hours, or under UV conditions for 500 hours. Throughout the aging processes, samples were characterized via colorimeter and FTIR spectroscopy to determine extent of color change and change in surface chemistry, respectively. With regards to FTIR analysis, the extent of oxidative aging of a particular material is often quantified by tracking the carbonyl content. Carbonyl species, which generally form upon reaction with ROS and the carbon polymer backbone, show prominent peaks between 1,600-1,900 cm^{-1}.[39, 40] The FTIR chromatogram shown in Figure 18 contains an overlay of FTIR samplings of the control material at various aging intervals. Under thermal conditions, the control sample showed very little change with regards to carbonyl formation, even after 1,500 hours of aging. As expected, UV aging of the epoxy samples showed significant oxidation of the sample, with moderately intense peaks appearing at 1,655 cm^{-1} and 1,721 cm^{-1}.

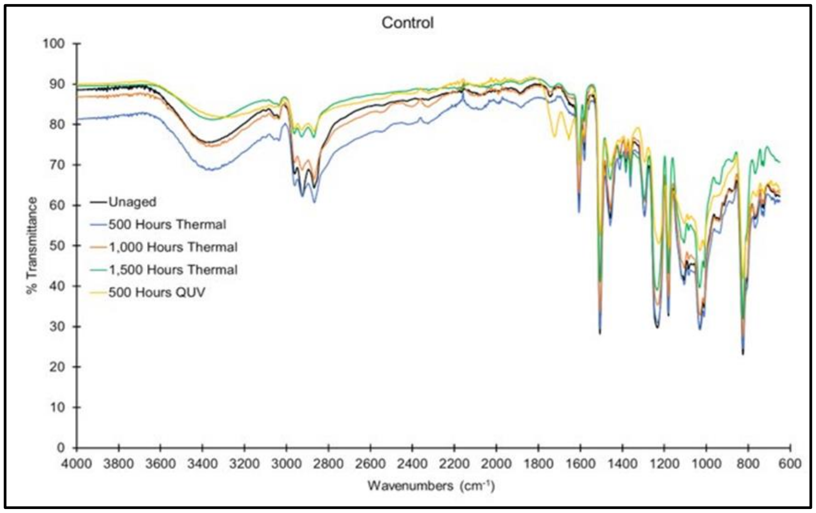
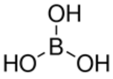
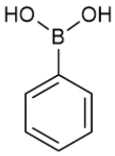
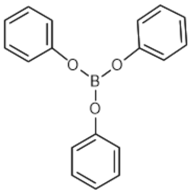
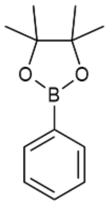


Figure 18. Overlay of FTIR samplings of the control material. Samples were aged either under thermal conditions for 1,500 hours or under UV conditions for 500 hours.

For comparative purposes, FTIR chromatograms of epoxy composites containing 5 mol% organoborons are shown in Figure 19. FTIR chromatograms for all samples are included in the appendix. Generally, all samples show the same behavior as the control sample; with the thermally aged samples showing very little peak formation in the carbonyl region after 1,500 hours, while the UV aged samples show considerable carbonyl peak formation at 500 hours. Of all the organoborons tested, no formulations prevented oxidation in the case of UV aging, while thermal aging results were inconclusive. FIR chromatograms of all epoxy systems tested are included in the appendix at the end of this report.

Table 11. Results from Soxhlet extraction experiments performed using water as the extracting solvent. Each epoxy formulation contained 5 mol% organoboron dopant. The value reported in the right column represents the weight percent material calculated from 100% organoboron mass.

% Extractables (H_2O, 72 h)

Name	Structure	Extracted (%)
Boric Acid (BA)		0.20078
Phenylboronic Acid (PBA)		-0.29383
Triphenyl Borate (TPB)		-0.42511
Phenylboronic pinacol ester (PAPE)		-0.81801

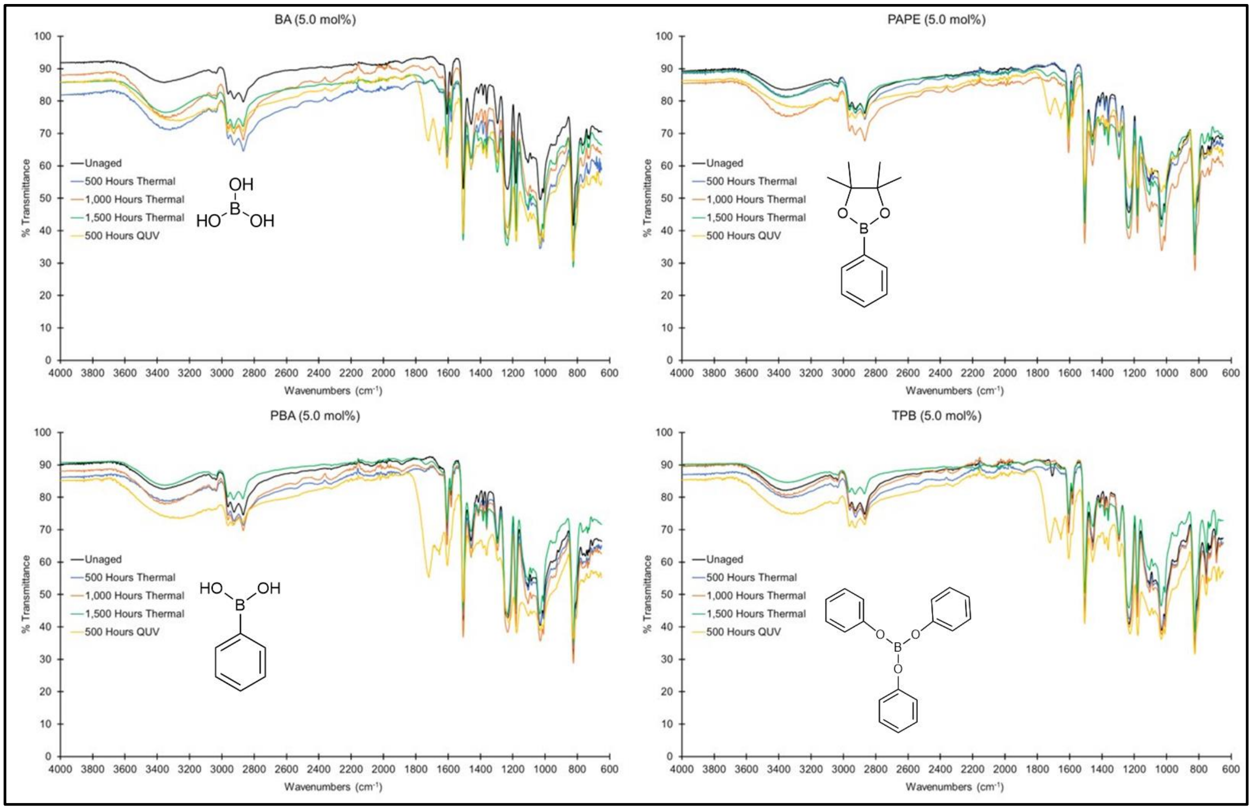


Figure 19. Overlay of FTIR samplings of epoxy composites containing 5 mol% organoborons. Samples were aged either under thermal conditions for 1,500 hours or under UV conditions for 500 hours.

At the molecular lever, carbonyl formation may lead to polymer backbone degradation and chain scission; at the macroscopic level, carbonyl formation often results in color changes (i.e. yellowing) to the material surface.[20] Colorimetric data is often described in discrete values of Delta E, which takes into account color changes in a three dimensional color space (shown in Figure 20).[41] Generally, Delta E values below 1.0 are imperceptible to the human eye, while values between 1-2 are perceptible to only the trained human eye. Values above 2.0 are easily discernible. Thus, colorimetric analysis was performed on the aged samples to determine the extent of yellowing at 1,500 h thermal aging and at 500 h UV aging, and the results are shown in Figure 21. Solid bars correspond to the samples that were aged under UV, while the striped bars correspond to the samples aged under thermal conditions.

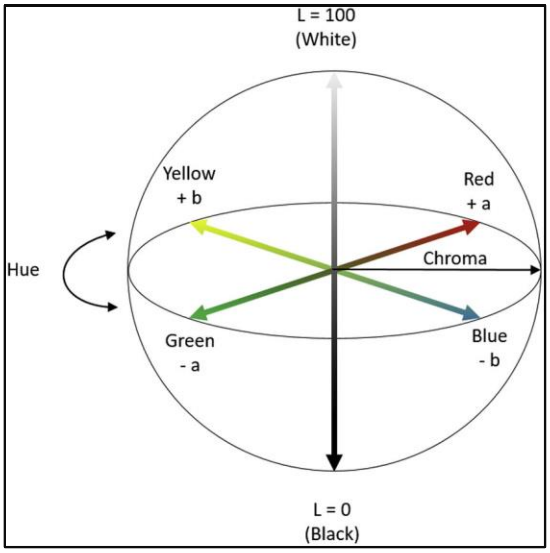


Figure 20. The three-dimensional L*a*b* color space, as defined by the Commission Internationale de l'éclairage's.

Analogous to the results measured via FTIR, the UV aged composites demonstrated significant oxidation as evidenced by their extensive discoloration. The lowest Delta E value for these materials was 28.86 (TPB 5.0 mol%), while the highest Delta E was 40.42 (BA 5.0 mol%). In some instances, the addition of an organoboron resulted in poorer color stability than the control sample (brown bar); however, one interesting trend is that color stability seemed to slightly increase at higher organoboron loading levels. The opposite trend seems to hold true in the case of the thermally aged samples, which show that increasing organoboron content resulted in higher delta E values (with BA being the only exception). Although the magnitude of color change for the thermally aged samples is significantly lower than their UV aged counterparts, all samples showed noticeable color change (i.e. evidence of oxidative degradation). Interestingly, the TPB 5.0 mol% sample showed significant color change in the thermally aged samples, with a Delta E value that was higher most UV aged samples (38.97).

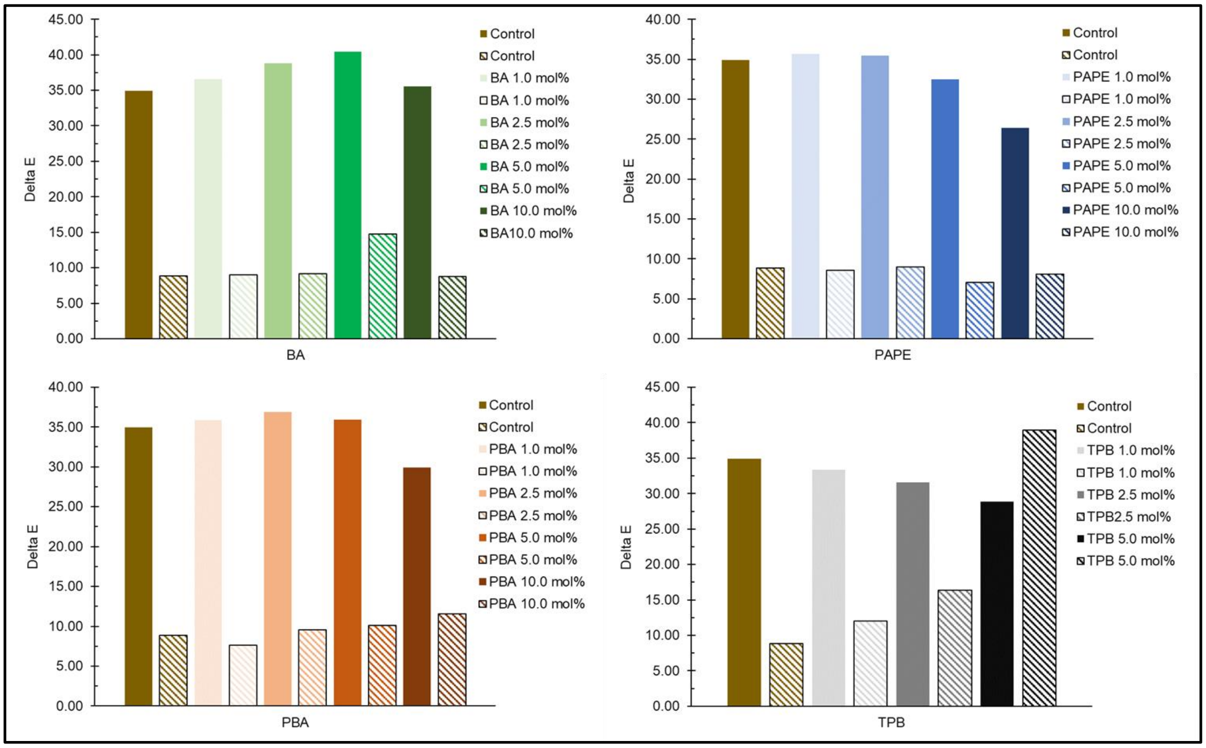


Figure 21. Colorimetry data of all aged epoxy composites. Samples were aged either under thermal conditions for 1,500 hours or under UV conditions for 500 hours.

ANTICIPATED OUTCOMES AND IMPACTS

Parts of this work will be published in either an American Chemical Society (ACS) or Royal Society of Chemistry (RSC) journal focused on coatings formulation or polymer degradation and stability. Furthermore, we hope to present the work at the 2023 Spring ACS National Meeting in Indianapolis, IN.

Although none of the organoborons tested in this work demonstrated antioxidant properties, there were some interesting outcomes that lend themselves towards further research. First, all organoborons tested in this project displayed negligible leaching tendencies, even under exceptionally harsh extraction conditions. A previous study demonstrated that this result also occurs even when changing the chemical identity of the crosslinker species. Thus, probing the utility of organoboron additives remains an attractive endeavor, as their incorporation into epoxy thermosets may yield advanced materials. This approach can also be extended to other thermoset polymer formulations, such as polyurethanes, polyureas, and silicones. Organoborons may also be used in thermoplastic formulations, where additive leaching is much more problematic.

NNSA and DOE's diverse mission areas would find usefulness in the multiple material applications described above. To reiterate, the nearly negligible leaching tendency, combined with the general benign health effects of organoborons and their ease of incorporation into epoxy thermoset chemistries, make organoborons an attractive chemistry to continue to investigate as a functional polymer additive used in thermoplastic/thermoset polymer applications. Boron-containing materials also hold interest in neutron attenuation or sensing applications, which ties to many of DOE/NNSA's mission areas.

CONCLUSIONS

A series of formulations were prepared by mixing organoborons (BA, PAPE, TPB, or PBA) into DEA or Epon 828 in concentrations ranging from 1.0-10.0 mol%. All organoboron formulations, with the exception of TPB, required only heat and magnetic stirring to yield shelf stable liquid precursors. In the case of TPB, a small amount of acetone was required to fully disperse the organoboron into the Epon 828, but removal of acetone under vacuum yielded shelf stable precursors for 1.0-5.0 mol% formulations. The 10 mol% formulation resulted in a poorly dispersed, gelatinous mixture. All formulations, with the exception of the 10.0 mol% TPB, yielded robust epoxy composites when cured with DEA (or Epon 828 in the case of BA). This process was based on previous SNL LDRD work that incorporated boric acid into a variety of amine based crosslinkers, which were subsequently cured to form robust epoxy networks that displayed relatively low leaching susceptibility.

The leaching performance of the cured epoxy samples was tested under dynamic conditions (Soxhlet extraction) over a 72-h period using water as the extraction medium. Soxhlet extractions resulted in negligible sample loss (>0.25%) in the case of BA, and a slight weight gain on all other organoboron sample. Thermal characterization of all samples demonstrated inconclusive results with regards to antioxidant performance via OIT testing, likely due to the crosslinked nature of the samples. Thermal degradation profiles of all samples, including the control sample containing no organoboron additives, showed nearly identical behavior in an inert environment. The degradation profiles differed significantly in an oxygen containing atmosphere, but no trends could be identified regarding antioxidant performance of the organoborons. Accelerated aging of the composite samples was performed under thermal and UV rich conditions for 1,500 h and 500 h, respectively. Heat aging of the samples showed very slight oxidation after 1,500 hours according to FTIR and color analysis, but these results were significantly magnified when aged under UV exposure. Based on FTIR and color analysis, accurate rankings of antioxidant performance of the organoborons tested in this study could not be made. However, color analysis did indicate that some formulations showed significantly worse performance when exposed to thermal conditions compared to UV exposure.

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APPENDIX

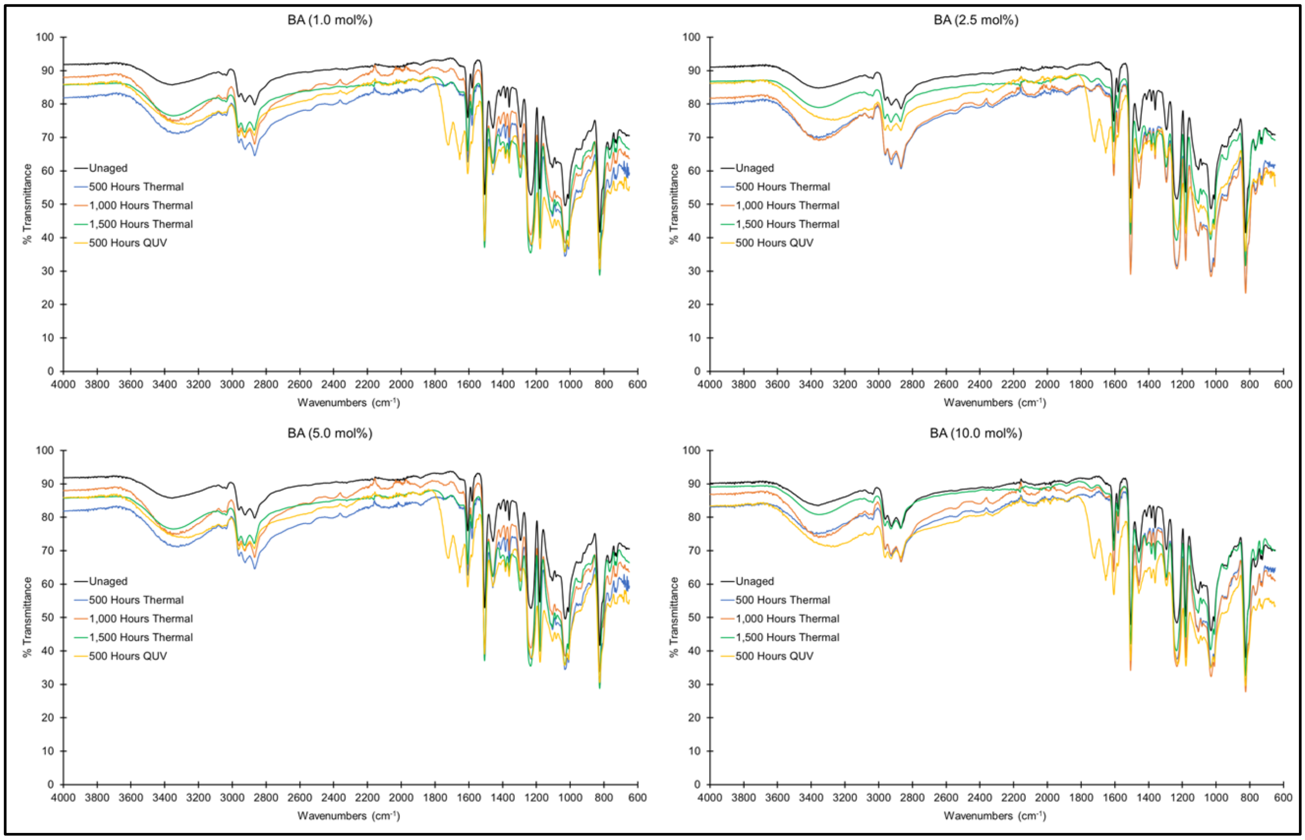

Figure 22. Overlay of FTIR samplings of epoxy composites containing BA with concentrations ranging from 1.0-10.0 mol%. Samples were aged either under thermal conditions for 1,500 hours or under UV conditions for 500 hours.

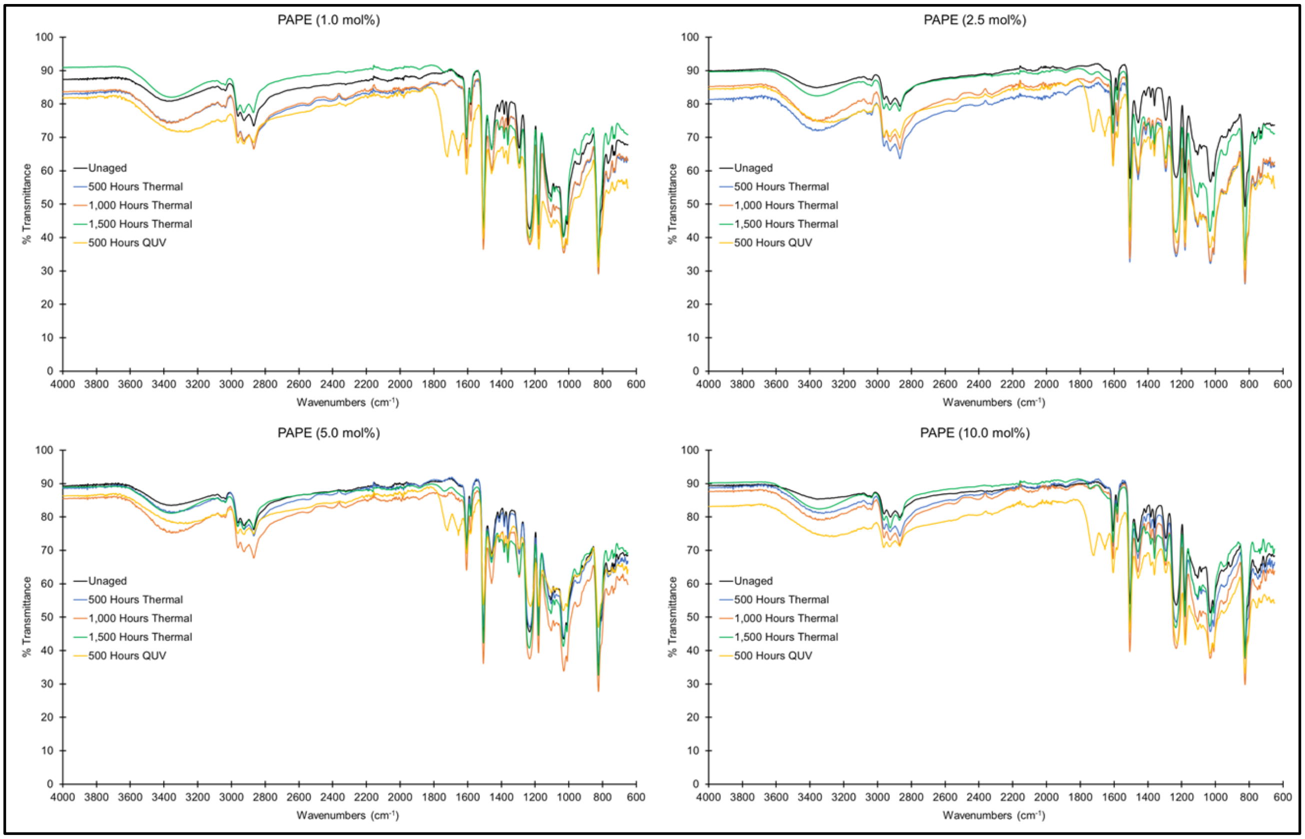

Figure 23. Overlay of FTIR samplings of epoxy composites containing PAPE with concentrations ranging from 1.0-10.0 mol%. Samples were aged either under thermal conditions for 1,500 hours or under UV conditions for 500 hours.

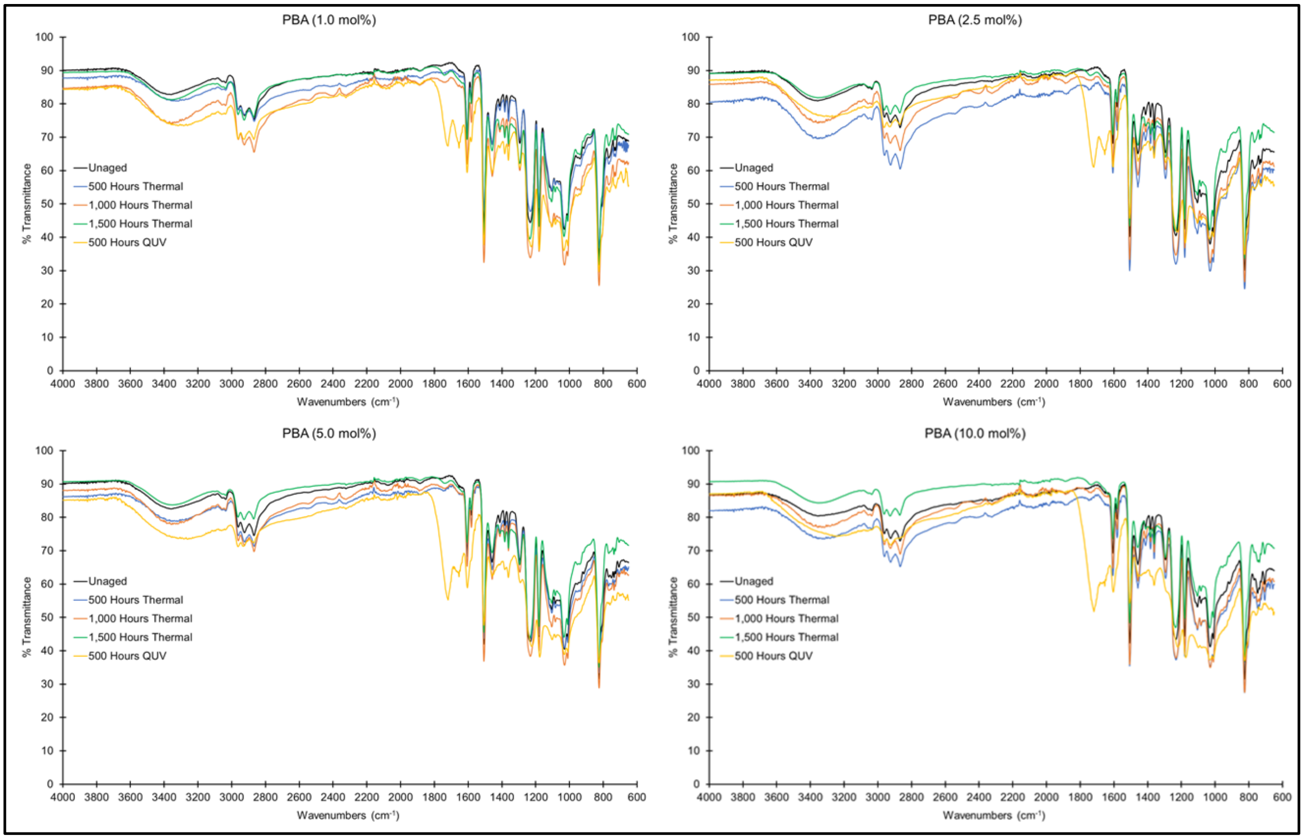

Figure 24. Overlay of FTIR samplings of epoxy composites containing PBA with concentrations ranging from 1.0-10.0 mol%. Samples were aged either under thermal conditions for 1,500 hours or under UV conditions for 500 hours.

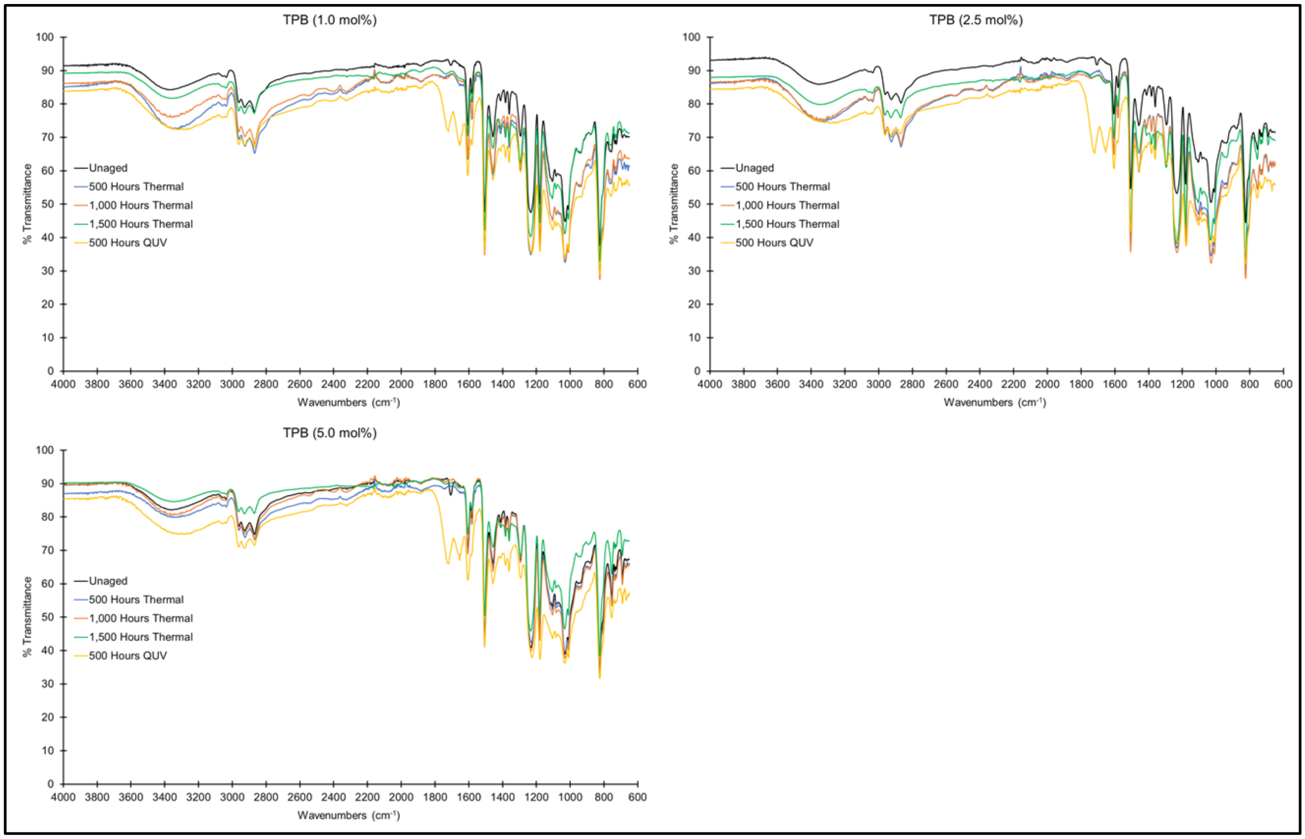

Figure 25. Overlay of FTIR samplings of epoxy composites containing TPB with concentrations ranging from 1.0-5.0 mol%. Samples were aged either under thermal conditions for 1,500 hours or under UV conditions for 500 hours.