SAND21XX-XXXXR

LDRD PROJECT NUMBER: 224480

LDRD PROJECT TITLE: Sustainable Functional Epoxies through Boric Acid Templating

PROJECT TEAM MEMBERS: Corey Parada (8634), Erica Redline (1853), Benjamin Juba (1852), Andre Benally (1852), Patti Sawyer (1853), Curt Mowry (1852), Cody Corbin* (8634)

ABSTRACT

Thermoset polymers (*e.g.* epoxies, vulcanizable rubbers, polyurethanes, etc.) are crosslinked materials with excellent thermal, chemical, and mechanical stability; these properties make thermoset materials attractive for use in harsh applications and environments. Unfortunately, material robustness means that these materials persist in the environment with very slow degradation over long periods of time. Balancing the benefits of material performance with sustainability is a challenge in need of novel solutions. Here, we aimed to address this challenge by incorporating boronic acid-amine complexes into epoxy thermoset chemistries, facilitating degradation of the material under pH neutral to alkaline conditions; in this scenario, water acts as an initiator to remove boron species, creating a porous structure with an enhanced surface area that makes the material more amenable to environmental degradation. Furthermore, the expulsion of the boron leaves the residual pores rich in amines which can be exploited for CO_2 absorption or other functionalization. We demonstrated the formation of novel boron species from neat mixing of amine compounds with boric acid, including one complex that appears highly stable under nitrogen atmosphere up to 600 °C. While degradation of the materials under static, alkaline conditions (our "trigger") was inconclusive at the time of this writing, dynamic conditions appeared more promising. Additionally, we showed that increasing boronic acid content created materials more resistant to thermal degradation, thus improving performance under typical high temperature use conditions.

INTRODUCTION AND EXECUTIVE SUMMARY OF RESULTS

Thermoset polymeric materials are commonly used in a sundry of different application spaces, such as adhesives, encapsulation compounds for sensitive electronic components, and as a matrix material for composites such as those used in aerospace. The most ubiquitous of the thermoset materials seen for these purposes are epoxies, which are typically composed of a difunctional epoxy resin and a di or trifunctional amine-based curing agent. When mixed and cured, these

Sandia National Laboratories is a multimission laboratory managed and operated by National Technology and Engineering Solutions of Sandia, LLC, a wholly owned subsidiary of Honeywell International, Inc., for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA-0003525.

compounds form a dense cross-linked network that provides robust chemical and mechanical material properties. These properties, which are very useful for the applications mentioned above and others, alternatively means that end-of-life environmental degradation rates can be exceedingly slow. This concept is particularly true for low surface area systems, which epoxies characteristically are used in. How surface area relates to environmental degradation time was recently evaluated with hydrocarbon-based polymers such as high-density polyethylene (HDPE), shown in Figure 1, which is significantly more difficult to degrade due to the lack of heteroatoms in its chemical structure.

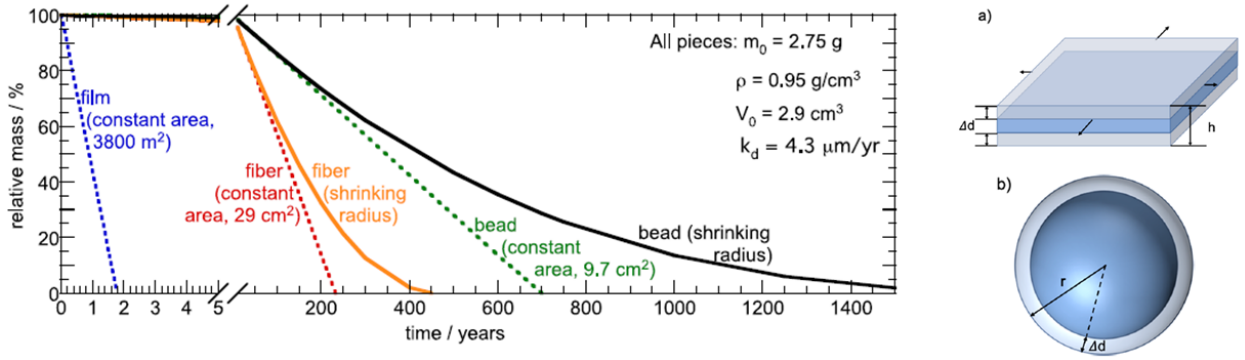


Figure 1. Comparison of predicted degradation profiles for HDPE pieces with the same mass, density, and SSDR but di□erent shapes (thin film, fiber, and bead). The dashed lines correspond to extrapolations assuming constant surface area; the solid lines correspond to a model which assumes the radius, and therefore the surface area, decrease over time.[1] (Borrowed directly from reference)

A clear correlation is seen by simple modeling of a sphere, which has the lowest surface area, and a thin film, which has the highest surface area. Results showed that the degradation time can be changed by 2-3 orders of magnitude, a significant improvement towards sustainability. Creating novel epoxy thermoset materials that can be aqueously stimulated to create higher surface higher would lower their persistence in the environment.

Previous SNL work back in 2010 utilized a molecule that had both epoxy and amine functionality in a single entity, along with the acidic triprotic compound phosphotungstic acid (PTA), to create a robust material with a uniformly dispersed high Z filler. The authors were successful and attributed to the dispersion uniformity to a coulombic acid/base reaction between the amine of the epoxy molecule and the acidic protons of the three -OH groups on the PTA (Figure 2 - Top). Based on this success, we wished to utilize a simple triprotic acid, boric acid, to achieve a similar coulombic result but with common curing agents used in epoxy formulations (Figure 2 – Bottom).

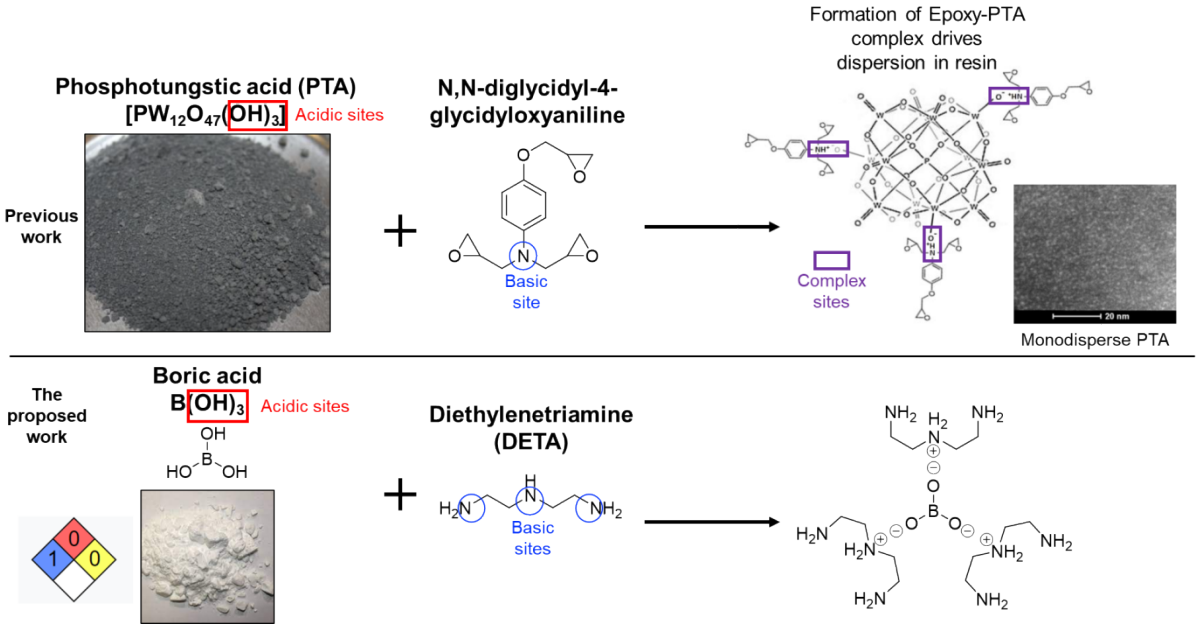


Figure 2. Top: Previous SNL work that combined PTA with a multifunctional epoxy molecule to form a tris(N,N-diglycidal-4-glycidaloxyanilinium) phosphotungstate complex. Inset is TEM image showing homogenous dispersion with scale bar at 20 nm. Bottom: Proposed concept using boric acid as a template with diethylenetriamine, a common curing agent used with epoxy resins.[2]

If the curing agent in question has multiple functional groups present to ring-open an epoxy ring for curing after complexation with the $B(OH)_3$, a curing agent is possible that has a removable molecule (borate) that can be extracted under neutral-to-basic conditions. Such a phenomena would happen at the surface of the bulk epoxy and slowly work its way in to form a porous thermoset that, with time, should see expedited degradation due to enhanced surface area (Figure 3).

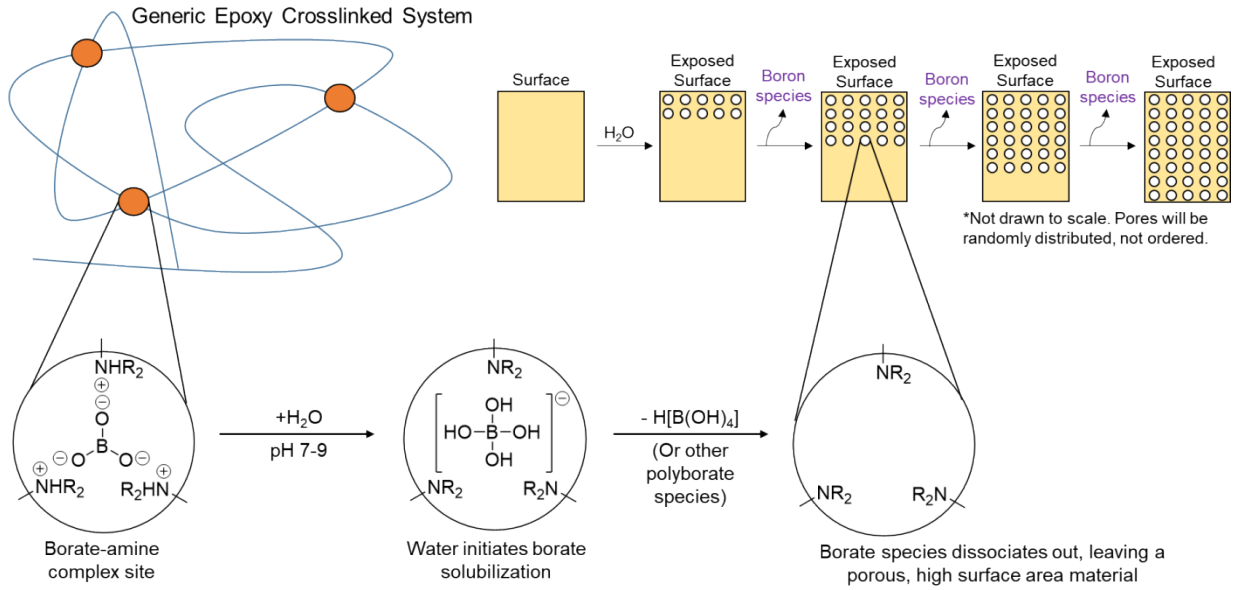


Figure 3. Generic diagram of a cross-linked epoxy system and the borate template active sites. Neutral-to-slightly basic water deprotonates ammoniums and forms a borate complex ion, which can then migrate out of the system from the surface. This process continues over time to yield a high surface area cross-linked system.

Previous work with starting materials of polyurethane thermosets, isocyanates, was attempted with boric acid and minerals acids to yield porous polyurea networks.[3] The boric acid, however, was determined to merely be a hydrating intermediate and was not ultimately bound within the final polymeric structure. Boric acid has also been esterified with polyols for the purpose of creating less combustive polyurethane materials[4], since borates are known to be a flame retardant.[5] And recently, amine-cured epoxies were surface-modified using boronic acids to form dioxazaborocanes.[6] This project investigated whether three common amine-based curing agents, diethylenetriamine (DETA), diethanolamine (DEA), and a trifunctional polyetheramine (T-403) could be mixed neat with boric acid to form such complexes, and to evaluate their aqueous degradation behavior once cured into EPON 828 epoxy resin.

DETAILED DESCRIPTION OF RESEARCH AND DEVELOPMENT AND METHODOLOGY

1. Materials

Hexane (ACS reagent, >99.5%), methanol (ACS reagent, >99.5%), ethanol (EtOH, denatured, reagent grade), acetone (ACS reagent, >99.5%), 2-propanol (IPA, ACS reagent, >99.5%), 1-propanol (ACS reagent, >99.5%), 2-butanol (ReagentPlus, >99.0%), 2-methyl-2-butanol (ReagentPlus, >99.0%), ethyl acetate (EtOAc, ACS reagent grade, >99.5%) acetonitrile (ACS reagent, >99.5%), sodium hydroxide (ACS reagent, >97%), boric acid (>99.5%), diethanolamine (DEA, puriss, >99.0%, ACS Reagent grade), diethylenetriamine (DETA, 99%,), and trimethylolpropane tri(poly(propylene glycol), amine terminated) ether (T-403), were purchased from Sigma-Aldrich and used as received. Deuterated solvents such as chloroform (CDCl3), methanol (CD_3OD), and dimethyl sulfoxide (d-DMSO) were purchased from Sigma-Aldrich and used as received. Methyl tert-butyl ether (MTBE, HPLC Grade >99%) was purchased from Alfa Aesar 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 (3.31 ppm for CD3OD) or TMS. Samples were prepared by dissolving the material in CDCl3 or CD3OD (5%, w/v) and charging this solution to a 5 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 64 scans at 0.482 cm-1 resolution.

2.3. Differential Scanning Calorimetry (DSC)

The thermal properties of the cured epoxy samples were measured using a TA Instruments Q-200 DSC. Approximately 3.0–10.0 mg of cured sample was hermetically sealed in an aluminum pan and heated up to 180 °C with a heating rate of 10 °C/min and kept for 1 min to keep a consistent thermal history for the melting process. And then, the samples were cooled to room temperature at a cooling rate of 10 °C/min.

2.4. Thermogravimetric Analysis (TGA)

TGA experiments were performed using either a TA Instruments Q5500 TGA or a Q5000 TGA, each equipped with an IR heater. Runs were performed under dry nitrogen gas with a flow rate of 25 mL/min, and samples were heated from 28.75 to 500 °C using a heating ramp rate of 10 °C/min.

2.5. Optical Microscopy

Optical microscopy was performed on a Keyence VHX-5000 ultra-depth-of-field microscope equipped with VH-ZST Dual Objective Zoom lens and a VHX-S550E mechanized sample stage. All images were processed using Keyence VHX-5000 Software Version 1.6.1.0.

2.6. LECO C/S

C/S analysis was performed on a LECO C/S 844 Interstitial Analyzer. A quality control (QC) sample was measured to verify the analyzer was calibrated correctly. The QC was run before, during, and after the samples. Samples were placed in ceramic crucibles with Iron flux and flux of a special metals blend provided by LECO (LECOCell II) for C/S analysis. The flux aided in melting the samples allowing the combustion to convert any carbon or sulfur to gas for analysis.

2.7. LECO ONH

ONH analysis was performed on a LECO ONH 836 Interstitial analyzer. Samples were placed in nickel capsules to aid in melting, then placed in a graphite crucible with graphite powder to convert any oxygen to carbon monoxide or carbon dioxide for analysis. The instrument was calibrated with high oxygen and hydrogen weight percent standards. Different quality control (QC) samples were measured to verify the analyzers were calibrated correctly. The QC's were run after the calibration, during the run, and after the run. All the QC's are well within the allowed range of the given value.

2.8 ICP-OES

Samples were tested using a Perkin Elmer (Groton, CT) Avio 500 ICP-OES. The instrument parameters include RF power: 1500 W, plasma flow: 15 L-Ar min−1, nebulizer flow: 0.7 L-Ar min−1, and auxiliary gas flow: 0.2 L-Ar min−1. Samples were analyzed along with standard elemental reference materials (Inorganic Ventures).

Preparation of Boric Acid-Amine Mixtures

Boric acid-amine mixtures were prepared using five different volume percent concentrations of boric acid (1.0, 2.5, 5.0, 10.0, and 20.0) via the following procedures.

The following procedure is representative for all DEA mixtures and was performed within a fume hood. To a dry 150 mL beaker, equipped with a magnetic stir bar, were charged 50.0 mL of DEA and 0.7175 g of boric acid. The beaker 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 overnight, after which the beaker was removed from heat. After cooling to room temperature, the mixture was transferred to a glass jar and capped tightly with a lid.

Aliquots of the liquid mixtures were taken and characterized via ^{11}B NMR, ^{1}H NMR, and ATR-FTIR without further purification.

For the T-403 samples, 40.0 mL of T-403 were used instead of 50.0 mL. All other steps were performed as described above.

For DETA samples, the previous procedure was performed at room temperature. After transferring the mixture to a glass jar, a white precipitate was observed to form within the solution over a period of several days. To facilitate further precipitation, the mixture was then sonicated (Branson 8510) for 30 minutes at 60 Hz, after which a significant amount of white solid was observed to precipitate from solution.

Trituration of Boric Acid-Amine Complexes from Mixtures

Boric acid-amine complexes were precipitated and/or triturated in order to remove excess amine content and determine the chemical structure of the boric acid-amine complex. Generally, mixtures were precipitated in a moderately polar, aprotic solvent and mixed via high-speed vortex mixing for several minutes. For DETA samples, MTBE was used to triturate the solid formed after sonication of the liquid mixture. For the T-403 and DEA mixtures, aliquots of the liquid mixture were added directly into vials containing acetone and a 50:50 (v:v) ethyl acetate:acetone mixture, respectively.

After mixing via vortex mixer, the dispersed solid was compacted via centrifuge, and the liquid layer was decanted. This process was repeated several times until a white solid was obtained. Residual solvent was removed via high vacuum at 50 °C, and the resulting white powder was transferred to a scintillation vial and characterized via ^{11}B NMR, ^{1}H NMR, ATR-FTIR, TGA/DSC, and elemental analysis.

Elemental Analysis Sample Preparation

Samples for LECO elemental analysis were quickly weighed directly from the vial and analyzed immediately after. ICP-OES samples were dissolved in DI water. 0.1 g samples were dissolved in 50 mL of water and then diluted an additional 10 times with water. Samples were noted to be extremely deliquescent.

Preparation of Epoxy Samples

Epoxy composites were prepared using the following procedure, which is representative. Epoxy samples of each boric acid-amine mixture were prepared by first heating the boric acid-amine complex and EPON 828 in an oven (Memmert UF-110 Plus) set to 70 °C. Meanwhile, disposable aluminum pans and glass slides were prepped by first cleaning with acetone, followed by drying under compressed air and then placing in the oven to equilibrate to 70 °C. After all materials were

equilibrated to 70 °C, approximately 5.0000 g of EPON 828 was transferred to an aluminum mold via pipette, which was subsequently placed back into the oven for 30 minutes. Subsequently, the aluminum mold containing the EPON 828 liquid was quickly removed from heat, zeroed on a balance, and an equivalent of boric acid-amine complex (based on stoichiometric equivalent of pure curing agent) was quickly transferred via pipette. The mixture was stirred vigorously for approximately 2 minutes, and a small sample was removed and coated onto a glass slide. Both the glass slide and the aluminum mold were then placed in the oven to cure for 24 hours at 70 °C. After curing, the aluminum mold was removed and discarded, and the sample was stored for further analysis.

Solvent Swelling/Extraction of Epoxy Samples

To determine the cured epoxy material's susceptibility towards degradation, solvent swelling and extraction experiments were performed under a variety of conditions. For solvent swelling experiments performed under static conditions, a clean glass jar was filled with approximately 50.0 mL of a pH 9.0 (± 0.10) KOH aqueous solution, whereby a glass slide coated with the cured epoxy was submerged into the solution. The jar was tightly capped and stored at room temperature in the dark. A separate experiment was also performed using EtOH instead of the aqueous solution.

In both series of experiments, samples were soaked for 7-day intervals then removed and analyzed via high resolution optical microscopy using the following method. After soaking for 7 days, the sample was removed from the jar, and gently rinsed with DI water then subsequently air dried. The glass slide was then placed on a white background and analyzed via optical microscopy. Images were captured either individually or using the photo stitching capability within the Keyence software**.** This process was repeated for a 6-week period.

Dynamic solvent extraction experiments were performed via Soxhlet extraction. Cured epoxy samples were ground into powders using a Retsch Mixer Mill 500 Nano set at 20 Hz for 1 hour, using a 20 mm stainless steel ball as the grinding media. The powder was transferred into a tared glass fiber thimble and weighed prior to the extraction process. Soxhlet extractions were performed under refluxing EtOH for 72 hours, after which the extraction solvent was removed and concentrated via rotary evaporation. The cured epoxy samples were dried under vacuum, removed from the glass fiber thimble, then weighed to determine mass loss.

RESULTS & DISCUSSION

Synthesis and Characterization of Liquid Boric Acid-Amine Mixtures

1. Synthesis of Boric Acid-Amine Mixtures

Boric acid-amine mixtures were prepared under neat conditions using either DEA, DETA, or T-403 as the reaction media. Five formulations for each crosslinker were prepared, with the boric acid content ranging from 1.0 – 20.0 volume percent of the formulation. Actual masses of boric acid used to prepare each solution are tabulated in Table 1. As described in the Experimental section above, 50.0 mL solutions of DEA and DETA were prepared, but in the case of T-403, 40.0 mL solutions were prepared.

Table 1. Boric acid volume percent, provided in grams, for each formulation of amine prepared

	1.0 vol% (g)	2.5 vol% (g)	5.0 vol% (g)	10 vol% (g)	20 vol% (g)
T-403	0.5740	1.4352	2.8703	5.7405	11.4801
DEA	0.7175	1.7944	3.5860	7.1754	14.3539
DETA	0.7175	1.7938	3.5885	7.1760	14.3521

Preparation of the DETA mixtures were carried out at room temperature, due to the low viscosity of the DETA starting material. Reaction progress could easily be monitored by visually tracking the disappearance of boric acid, and complete disappearance was observed to occur within 12 hours. For all DEA and T-403 boric acid mixtures, elevated temperatures were required to overcome the high viscosity of the starting materials and achieve adequate mixing. Similar to the DETA formulations, all DEA and T-403 systems smoothly formed their homogenous counterparts at elevated temperature, and reaction progress could similarly be monitored by visual observation of the disappearance of boric acid (< 12 h).

Shelf stability of the crosslinker/boric acid mixtures were found to be highly dependent upon the chemical structure of the crosslinker. In the case of all DEA and T-403 mixtures, removal from heat after mixing resulted in a clear liquid that was shelf stable at room temperature. Although all DEA and T-403 mixtures were homogenous, there appeared to be a direct correlation between solution viscosity and boric acid loading. Generally, mixtures containing higher boric acid concentrations displayed noticeably higher viscosities at room temperature. Compared to the DEA and T-403 mixtures, which were indefinitely stable at room temperature, all DETA mixtures above 1.0 vol% boric acid yielded a white precipitate after several days. Upon sonication of the mixtures, a significant amount of white precipitate was observed in the form of a waxy solid. The amount of solid formation appeared to increase with increasing boric acid concentration. Trituration of the waxy solid with MTBE (a moderately polar, non-hygroscopic aprotic solvent) gave a fine white powder that was moderately hygroscopic and soluble in protic solvents.

The presence of a waxy solid for the DETA systems, which when characterized via ^{11}B NMR confirmed the presence of boron (discussed below), raised our suspicions that the DEA and T-403

systems may also contain solid complexes. Thus, samples of T-403 boric acid (5 vol %) and DEA boric acid (5 vol%) were precipitated into non-polar, aprotic solvents to determine if indeed a solid complex of these materials existed. When the T-403 mixture was precipitated into acetone, a white solid formed, which upon further trituration and drying yielded a fluffy white powder that was readily soluble in protic solvents. This material was also moderately hygroscopic, as the white solid would quickly transform into a waxy, clear gel in the presence of atmospheric moisture (i.e. sitting on a benchtop). In the case of the DEA mixture, a mixture of 50:50 ethyl acetate:acetone was found to be more effective, due to ethyl acetate's lower hygroscopicity. While the DETA and T-403 solids were both moderately hygroscopic, the DEA solid was readily hygroscopic and would transform into a waxy solid within minutes of being introduced to atmosphere.

Due to the presence of atmospheric moisture, it was observed that using MTBE in the final trituration step would eliminate any clumps in any of the aforementioned isolated solids. Drying the samples under vacuum resulted in a free-flowing powder. It is recommended that long term storage of these solids should include storing under a dry N_2 environment or under a layer of MTBE or hexane to minimize exposure to moisture.

Characterization of Boric Acid-Amine Mixtures

To better understand the chemical nature of the boric acid-amine mixtures, both the liquid mixtures and the solid complexes were characterized via NMR (^{1}H, ^{11}B) and FTIR. Solubility testing was also performed on the solid complexes to determine their range of solubility. The solid complexes were further characterized via elemental analysis and DSC.

2.1 Characterization via NMR

The liquid mixtures and solid complexes of T-403 and DEA systems were characterized via ^{1}H and their spectra are shown below in Figures 4 and 5, respectively. For the T-403 based mixtures shown in Figure 4, the oligomeric nature of the crosslinker resulted in convoluted spectra of the starting material and reaction products; despite this, some insights could be gained by comparing the areas of interest (light green highlighted areas) in the reaction products to the starting materials. One of the most prominent differences lies in the aliphatic region between 1.00 and 1.20 ppm. For the T-403 starting material, there is a pronounced peak centered at 1.02 ppm showing a doublet of doublets (*dd*), and a second *dd* found slightly more downfield at 1.12 ppm. These peaks shift slightly downfield for the liquid product mixture, changing to 1.06 ppm and 1.13 ppm respectively. Also, the splitting patterns become slightly more pronounced, indicating a slight change in the chemical environments of the protons. The most notable difference occurs in the solid precipitate (top spectrum) where the doublet at 1.06 ppm shifts downfield to overlap with the peak at 1.16, which no longer has a *dd* splitting pattern but instead a triplet.

Another area of note is the multiplet centered at 3.00 ppm for the neat T-403 sample. This peak shifts slightly downfield in the liquid product (3.06 ppm) but has completely disappeared for the solid precipitate sample. Comparing the integrations of the region between 3.00 and 3.80 of all 3 spectra suggests that this peak has shifted more downfield into the unresolved series of peaks between 3.20- 3.50 ppm, but integrations in this region are unreliable due to the presence of the residual solvent peak at 3.31 ppm (e.g. the pronounced singlet in the top spectrum). Similarly, the multiplet at 3.60 ppm found in the neat T-403 and the liquid T-403 mixture has also disappeared; using the same argument above, comparison of the integrations suggest that this peak has shifted slightly upfield into the unresolved series of peaks, but this is inconclusive.

Downfield peak shifting is also observed in the region between 1.30 and 1.50 ppm, where a poorly resolved series of peaks (possibly two overlapping quartets) in the neat T-403 sample seems to shift slightly downfield and become even more poorly resolved in the liquid and solid T-403 samples. Integration of these peaks shows little difference in this region between all three spectra.

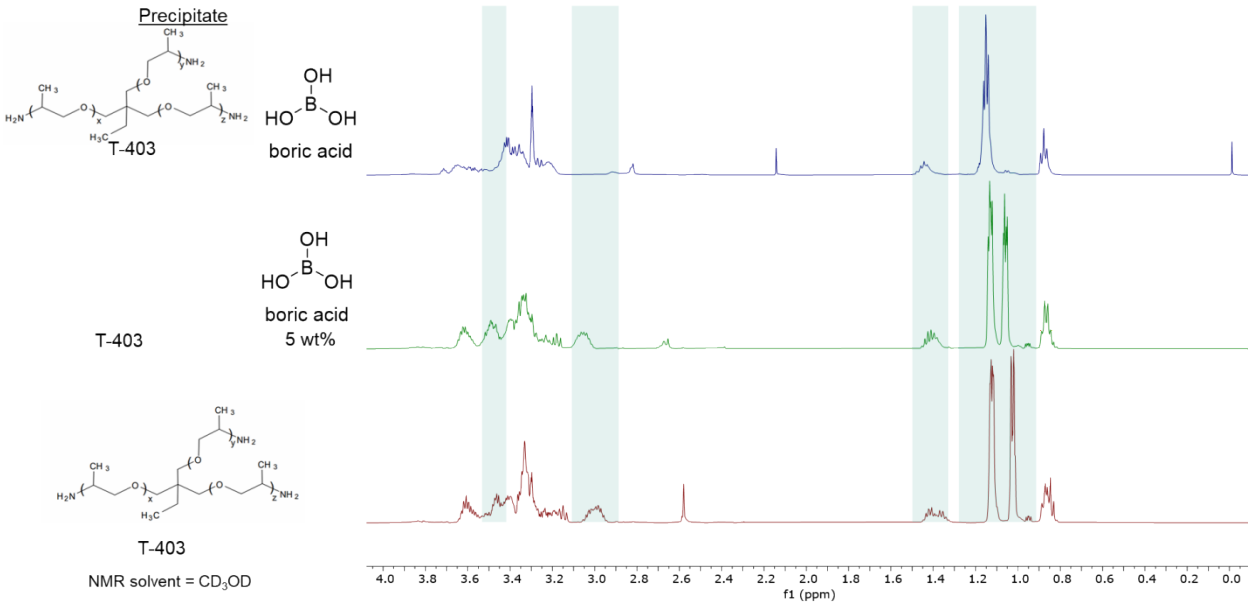


Figure 4. ^{1}H NMR spectra (500 MHz, CD_3OD, 23 °C) of T-403 (bottom), the liquid reaction product of T-403 and 5 vol% boric acid (middle), and the solid complex isolated from trituration of the liquid reaction product (top).

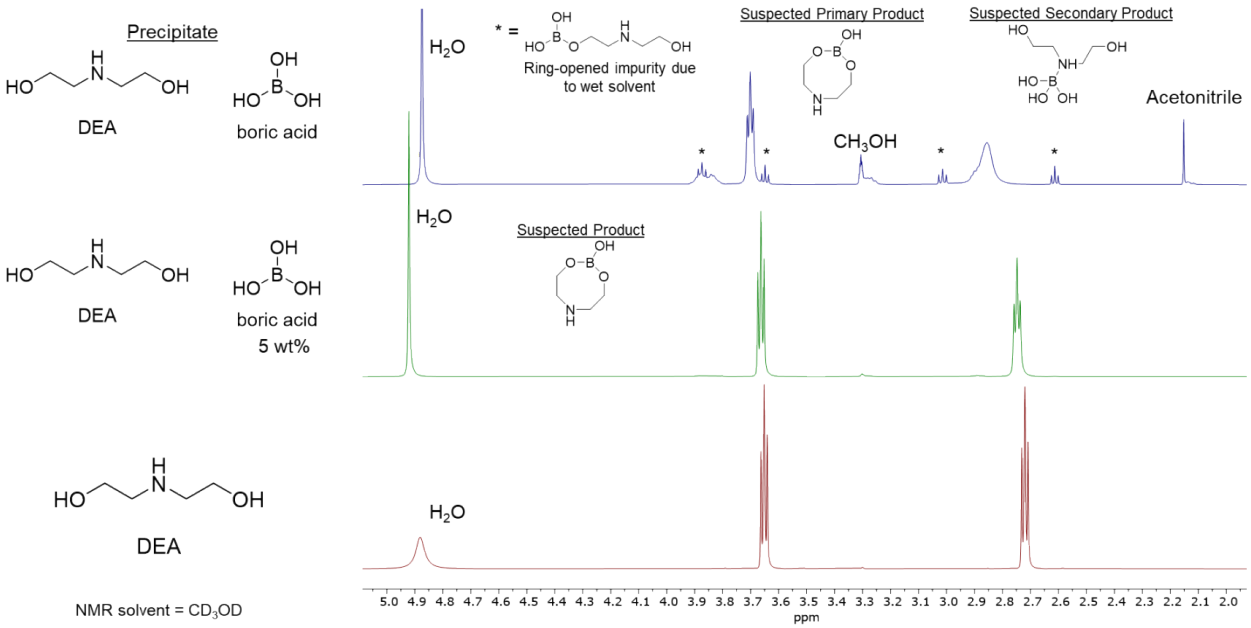


Figure 5. ^{1}H NMR spectra (500 MHz, CD_3OD, 23 °C) of DEA (bottom), the liquid reaction product of DEA and 5 vol% boric acid (middle), and the solid complex isolated from trituration of the liquid reaction product (top).

Whereas the T-403 series of materials were oligomeric in nature, the discrete structure of DEA resulted in cleaner spectra that are easier to interpret. Comparing the starting material and the liquid reaction product shows minimal differences in spectra, with the most significant being the change in the peak at 4.87 ppm. This peak shifts slightly downfield to 4.92 ppm for the liquid mixture, but becomes significantly more narrow and more intense. The very slight downfield shift of the triplets at 2.71 and 3.65 (shifting to 2.75 and 3.66 for the liquid mixture, respectively) indicate that these protons experience a very minor change in chemical environment. Thus, we propose that the liquid material consists solely of the cyclized structure shown in Figure 5, which has been reported previously in the literature.[7] Interestingly, however, the spectrum for the solid precipitate (Figure 5 top) indicates a number of differences between the solid and liquid states of the DEA- boric acid mixture. Primarily, the existence of a number of less intense triplets at 2.61, 3.02, 3.65 and 3.87 ppm indicate a linear structure, likely caused by the presence of moisture. During workup and NMR sample preparation, it was observed that the solid precipitate would change from a fine white powder to a waxy solid within minutes if left open to atmosphere; residual water in the CD_3OD could also affect this material. Correspondingly, we hypothesize that the presence of moisture could likely lead to the formation of various side products, from a linear, ring-opened impurity to a Lewis acid/base type product. By comparison, the solid precipitates from the T-403 and DETA samples were much less hygroscopic and more shelf stable than the DEA solid.

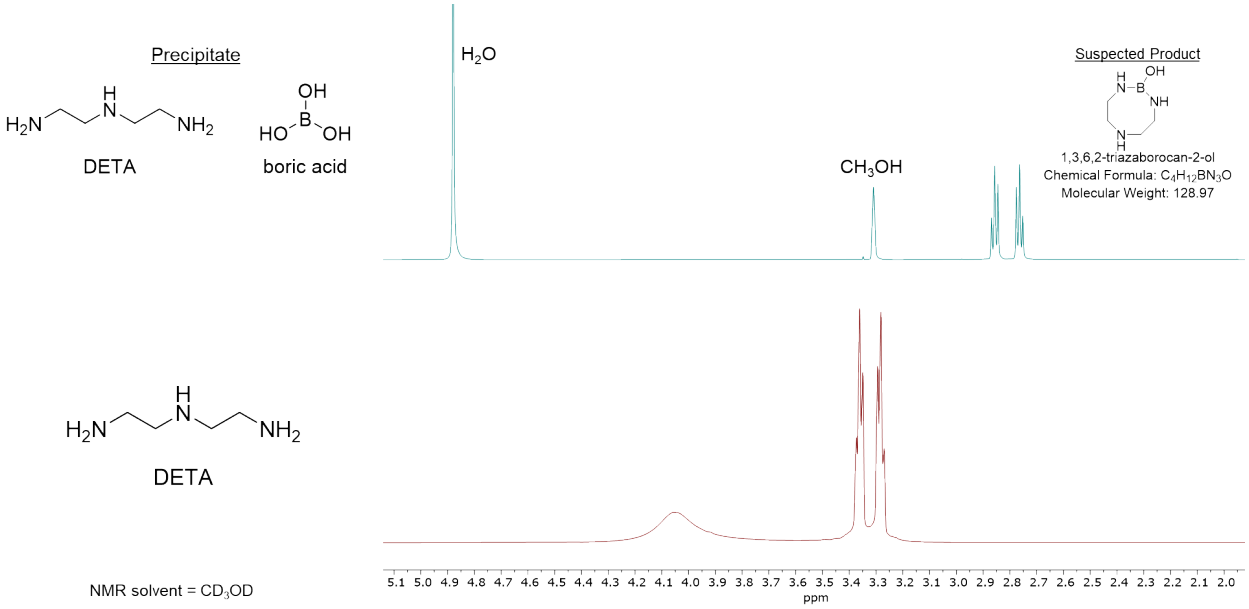


Figure 6. ^{1}H NMR spectra (500 MHz, CD_3OD, 23 °C) of DETA (bottom) and the solid precipitate formed from the reaction of DETA with 5 vol% boric acid. (top).

By far the simplest material to characterize via ^{1}H NMR was the reaction product isolated from the DETA mixture. This material, which precipitated from the liquid mixture of DETA and boric acid, was triturated with MTBE and found to be somewhat shelf stable in the presence of moisture. After drying, the resulting solid gave the top spectra in Figure 6, which is fairly clean and easy to interpret. Similar to the proposed structure in Figure 5, the crisp triplets and existence of only two peaks indicate a symmetrical molecule, which we believe to be the cyclic compound shown in Figure 6. Not shown in Figure 6 is the ^{1}H spectrum of the liquid layer (separated from the solid precipitate and characterized without further workup), which was found to be unreacted DETA.

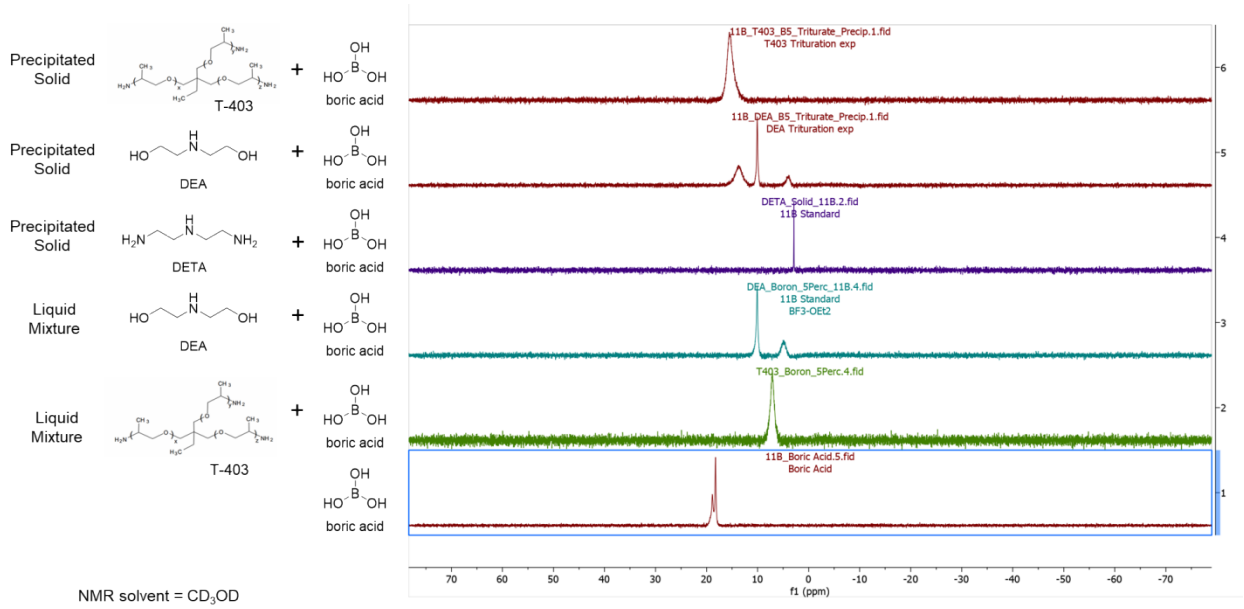


Figure 7. ^{11}B NMR spectra (500 MHz, CD_3OD, 23 °C) of boric acid and all relevant liquid mixtures/triturated solids.

In addition to ^{1}H NMR, ^{11}B NMR spectra were obtained to determine the chemical environment of the boron found in each sample; these are shown in Figure 7. For the boric acid starting material, an asymmetric peak at 18.83 and 18.19 was the most downfield, while the liquid mixture of T-403 and boric acid gave a single slightly broad peak at 7.11 ppm. The existence of a similar, slightly broad singlet is also observed for the solid T-403 precipitate (15.68 ppm, top spectrum) indicating that a single species is present in both materials. This observation allows for more structural information to be elucidated than just the ^{1}H NMR's, which were complex (due to the oligomeric nature of the T-403) and thus gave limited structural information.

In the case of the DEA liquid mixture, two peaks were observed and have been seen previously in the literature: a singlet at 4.89 and a more intense singlet at 10.06 ppm.[7] The presence of two peaks of differing intensities conflicts with our hypothesis that a single cyclic compound exists in the liquid phase, but the hygroscopic nature of the compound does not rule out the possibility that residual moisture from the NMR solvent or atmosphere could cause ring opening of the cyclic compound. This ring opening reaction from residual or atmospheric moisture may also be occurring in the solid DEA sample, as the ^{11}B spectrum suggests that up to three boron species exist, further adding to the complexity of structural analysis.

In the case of the precipitated DETA sample, a single narrow peak indicates the presence of a single species, which we hypothesize to be the cyclic structure proposed in Figure 6. Similar to

Figure 6, an ^{11}B NMR of the liquid layer in the DETA sample did not result in any measurable signal, lending further evidence towards the conclusion that the liquid layer contained only unreacted DETA.

2.2 Characterization via FTIR

In combination with ^{1}H and ^{11}B NMR, structural analysis of the liquid and solid components was performed using FTIR, which are shown below in Figure 8.

FTIR analysis of each material provided some insight to the chemical structure of the liquid mixtures but was hampered by poor peak resolution and the propensity for boron bond frequencies to fall within the fingerprint region (<1,500 cm^{-1}).[8-12] Significantly, the presence of systematic increases in boric acid concentrations resulted in increased intensity in frequencies associated with B-O and B-N stretching (1330-1350 cm^{-1}) in the T-403, DEA, and DETA materials.[7, 13] Interestingly, the presence of a broad peak within the region typically associated with O-H stretching (3,200- 3,600 cm^{-1}) is not present in the T-403 and DETA samples. The DEA mixtures, however, were the exception to this, but only a slightly increase in peak intensity is observed upon reaction with boric acid, even at relatively high boric acid loadings.[9, 13]

The disproportionate change in peak intensity (i.e. significant increase in B-N and B-O stretching peak intensity and slight increase in O-H stretching intensity), gives further evidence towards the existence of covalent B-N and B-O species, rather than Lewis acid-base species, for the T-403, DEA, and DETA mixtures. In the case of the liquid DETA material (1.0% boric acid) and the precipitated DETA materials (boric acid content $\leq$ 2.5%), the disappearance of the weak N-H_2 scissoring mode (1,600 cm^{-1}) and the appearance of strong bands around 1,350 cm^{-1} (B-N stretching) gives further evidence of the formation of covalent bond formation.[13]

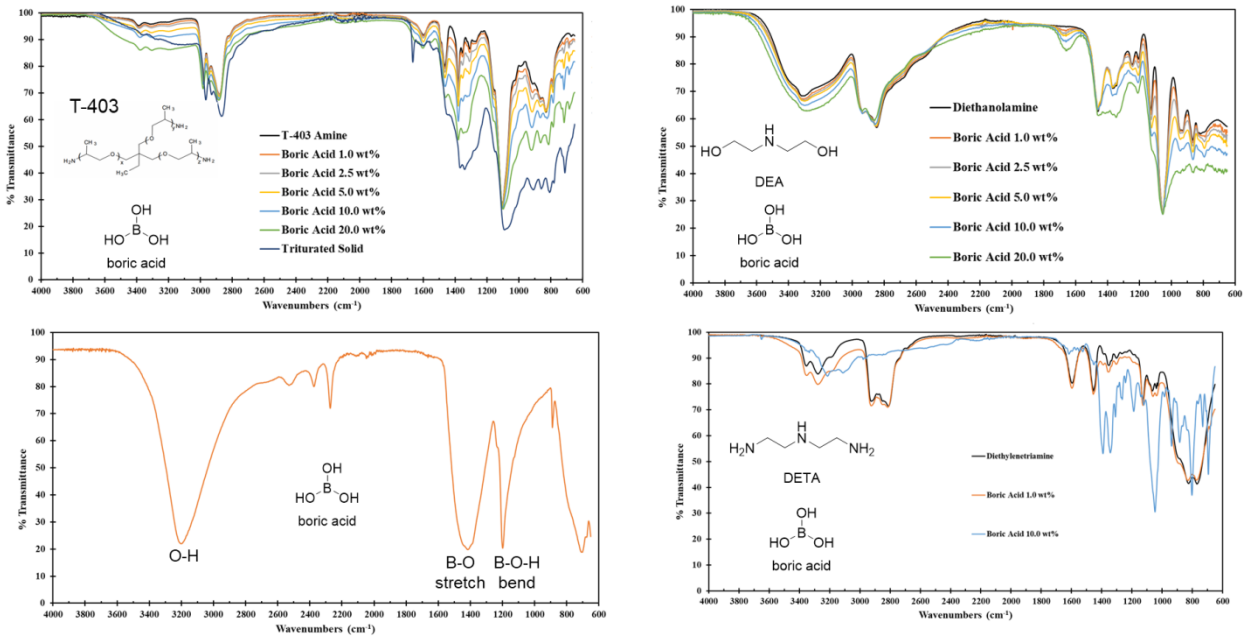


Figure 8. Clockwise from top left, FTIR chromatograms of: T-403 liquid mixtures and precipitate, DEA liquid mixtures, DETA liquid mixtures and solid precipitate, and boric acid starting material.

2.3 Characterization via TGA/DSC

Thermal analyses of the solid complexes were performed using TGA and DSC, and the resulting plots are presented below in Figure 9. For the DEA and T-403 materials, our suspicions of hygroscopicity were confirmed via TGA, as a significant portion of weight was lost in the region between 80-120 °C. This weight loss likely represents the loss of water, which accounted for 5-10% of the overall weight of the material. Originally, DETA showed much higher stability towards these lower temperatures as indicated by the orange line in Figure 9; however, a subsequent run using a larger sample showed a similar trend as that of the DEA and T-403 plots; namely, loss of ~5-10% water within 80-120 °C.

As the DETA material approached 150 °C, significant mass loss (20 wt%) was observed, which is supported by the significant endothermic peak in the DSC thermogram. This was not observed in the DEA and T-403 samples. Rather, the DEA and T-403 materials showed nearly constant mass loss (as indicated by semi-linear downward slope) between 150-350 °C, followed by a plateau beyond 400 °C. The final weight of both samples ended at just over 10% of their original mass. This trend was not observed for the DETA sample, as the material was measured to lose about 35% of its mass between the temperature range from 175 to 600 °C, with about 40 wt% of its original mass left at the end of the TGA run.

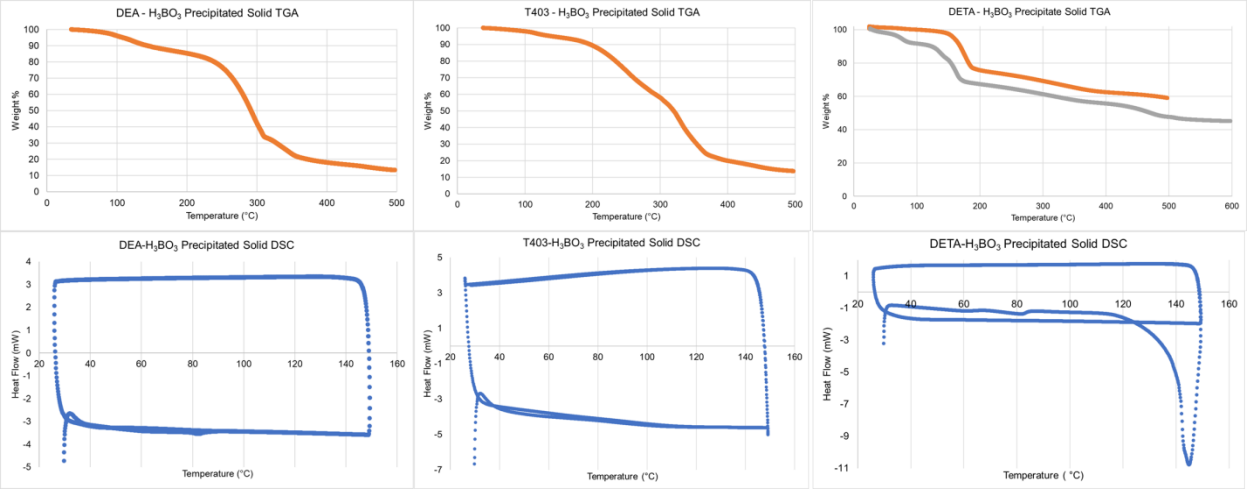


Figure 9. TGA and DSC thermograms of the solid complexes of DEA (left), T-403 (middle), DETA (right).

2.4 Characterization via Elemental Analysis

Solid precipitates of the T-403, DEA, and DETA materials were characterized for elemental composition, and the results for each material are tabulated below. These materials were found to be readily soluble in C_1 and C_2 alcohols and water, moderately soluble in C_3 alcohols, and slightly soluble in C_4 alcohols. They were insoluble in aliphatic/aromatic solvents, halogenated solvents, ethers, esters, ketones, and amides.

Generally, boron content was measured via ICP-OES and all remaining elements were measured using LECO combustion analysis. Notably, mass closure was well below 100% for all samples, indicating that moisture was readily present on all samples during analysis. Due to this artifact, the oxygen and hydrogen content reported below is likely artificially inflated and the BCN content is deflated.

Table 2. DETA Composition Results in Weight Percent.

DETA Precipitate	B	C	O	N	H	Sum
Average	**14.60%**	**19.7%**	**28.5%**	**5.20%**	**2.25%**	**70.29%**
Std Dev	0.486%	0.86%	1.56%	0.77%	0.20%	

Table 3. DEA Composition Results in Weight Percent.

DEA Precipitate	B	C	O	N	H	Sum
Average	**7.393%**	**41.0%**	**13.3%**	**4.89%**	**3.86%**	**70.40%**

Std Dev	0.0669%	1.8%	2.3%	0.63%	0.50%	

Table 4. T-403 Composition Results in Weight Percent.

T-403 Precipitate	B	C	O	N	H	Sum
Average	**4.074%**	**49.3%**	**13.6%**	**4.38%**	**4.19%**	**75.51%**
Std Dev	0.0525%	1.0%	0.93%	0.23%	0.24%	

3. Epoxy Composites- Curing Behavior and Thermal Properties

Epoxy composites were formulated with each crosslinker/boric acid complex added at the suggested stoichiometric equivalence of the neat crosslinker; for T-403, this was 42 parts per hundred of EPON 828. For DEA, this was 12 parts per hundred of EPON 828. The masses of each crosslinker-boric acid complex used in each epoxy composite are tabulated below; the mass of epoxy for each sample stayed constant at 5.00 grams (± 0.0050 g).

Table 5. Boric acid-amine formulations used, in grams, with EPON 828 epoxy resin to prepare 5 grams of total material

	0.0 vol% (g)	1.0 vol% (g)	2.5 vol% (g)	5.0 vol% (g)	10 vol% (g)	20 vol% (g)
T-403-Boric acid	2.1609	2.1553	2.1624	2.1636	2.1792	2.1550
DEA- Boric acid	0.6001	0.6070	0.6000	0.5996	0.5990	0.6026

Our first attempt to form epoxy composites with either DEA/boric acid or T-403/boric acid mixtures at room temperature resulted in poorly mixed, phase separated samples with poor mechanical stability. Even after curing at elevated temperatures for 24 hours, the resulting materials contained uncured domains (in the form of a sticky residue) and displayed a cloudy interface, rather than being optically transparent. Both properties are indicative of phase separation within the material. When both the epoxy and crosslinker component were heated before mixing, the resulting mixing process proceeded smoothly and resulted in good composite samples, with the exception of the T-403 formulations containing 10% and 20% boric acid. These formulations contained some uncured residue on the aluminum mold.

3.1 Epoxy Composites - Thermal Characterization

Thermal properties of cured epoxy composites of each DEA and T-403 formulation were analyzed via DSC and TGA. TGA results on DEA cured epoxies (performed in an N_2 environment) are tabulated in Table 6 and the plot is shown in Figure 10, showing the temperatures at which 10%, 50%, and 80% mass loss was achieved for each sample. As expected, increasing the boric acid content within a given epoxy network resulted in an increase in degradation resistance. The temperatures required to reach 10% mass loss differed within 1.0 °C for all boric acid containing composites, but as degradation proceeded, the samples containing lower boric acid concentrations showed exhibited slightly earlier degradation than their higher boric acid containing counterparts. The epoxy composite containing the highest amount of boric acid (20.0 vol %) began to plateau near 500 °C, but continued to lose mass until the run was terminated at 500 °C.

Table 6. TGA data for boric acid containing epoxy composites cured with DEA.

	0.0 vol% (g)	1.0 vol% (g)	2.5 vol% (g)	5.0 vol% (g)	10 vol% (g)	20 vol% (g)
T_{10} (°C)	372.34	375.52	376.52	375.42	376.29	376.62
T_{50} (°C)	403.51	407.87	411.26	410.41	412.20	417.53
T_{80} (°C)	431.80	437.37	439.42	441.12	451.80	> 500

TGA results on T-403 cured epoxies are tabulated in Table 4 and is also plotted in Figure 10. Similar to the DEA samples, the addition of boric acid directly correlated to higher thermal degradation temperatures, although the thermograms for the T-403 samples were not as clean as the DEA thermograms. As expected, increasing the boric acid content within the epoxy network each epoxy composite resulted in an increase thermal resistance towards degradation. Unlike the DEA samples, however, the temperature required to reach 10% mass loss varied significantly between all samples, but this variance became much lower as the samples approached 50% mass loss. As degradation continued beyond 50% mass loss, the variance increased significantly again. Interestingly, the epoxy composite containing a moderate amount of boric acid (5.0 vol%) did not reach complete decomposition even at 500 °C when the run was terminated, but the epoxy composites containing 10.0 and 20.0 vol% boric acid performed significantly better.

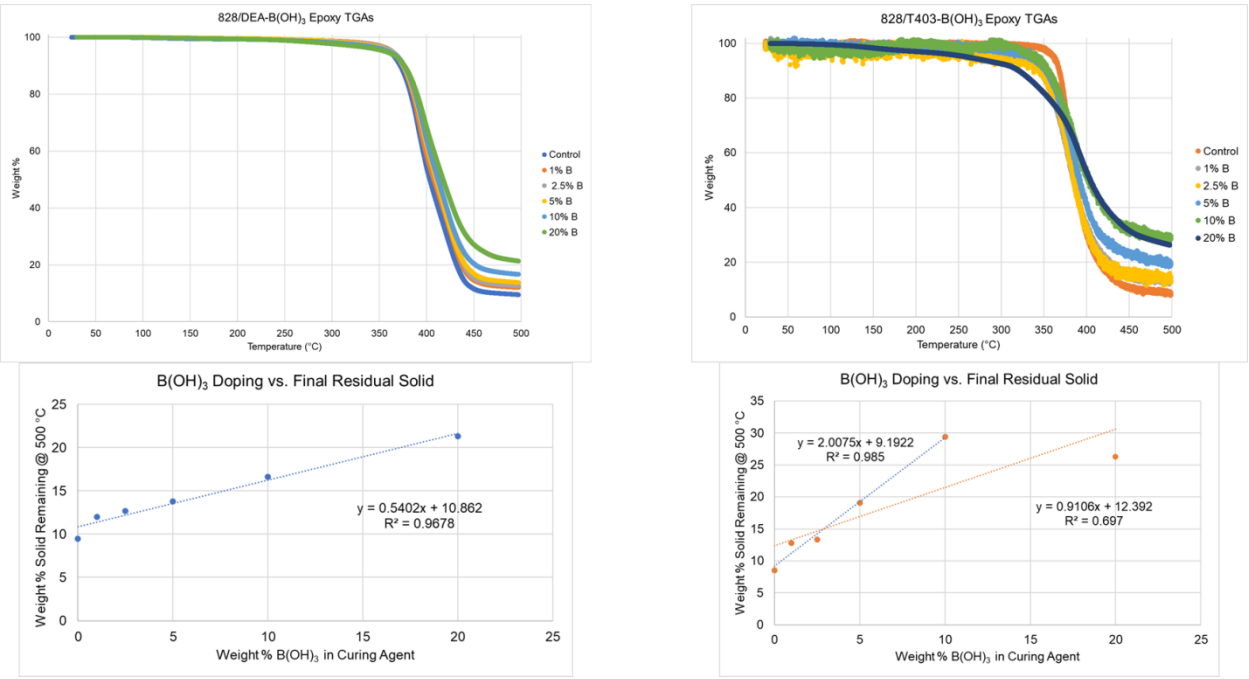


Figure 10. Clockwise from top left, TGA plots of DEA:$B(OH)_3$ cured epoxy composites, T-403:$B(OH)_3$ cured epoxy composites, corresponding wt:wt plots of initial boric acid to solid residue for T-403 mixtures, and corresponding wt:wt plots of initial boric acid to solid residue for DEA mixtures.

Table 4. TGA data for boric acid containing epoxy composites cured with T-403.

	0.0 vol% (g)	1.0 vol% (g)	2.5 vol% (g)	5.0 vol% (g)	10 vol% (g)	20 vol% (g)
T_{10} (°C)	368.05	346.67	346.41	354.43	355.03	320.83
T_{50} (°C)	387.04	384.42	384.90	390.79	403.28	404.35
T_{80} (°C)	414.216	426.598	419.99	491.37	> 500	> 500

DSC measurements were also performed on the cured networks, and representative sample thermograms are plotted in Figures 11 and 12 below. One of the most significant factors from the DSC data below shows the presence of a large endotherm in the first heating cycle for both

materials, indicating the presence of uncured material in the composite. In the case of T-403 samples, these are likely unreacted chain ends that were vitrified during the first curing cycle. Unreacted domains were expected for these composites due to the presence of a sticky residue on the sample surface after curing. This observation was unexpected for the DEA systems, however, as the samples did not leave any residue upon removal from the curing pan.

During the second heating cycle, the glass transition temperature of the fully cured samples was found to be around 80 °C for the T-403 cured samples, and around 85 °C for the DEA cured samples.

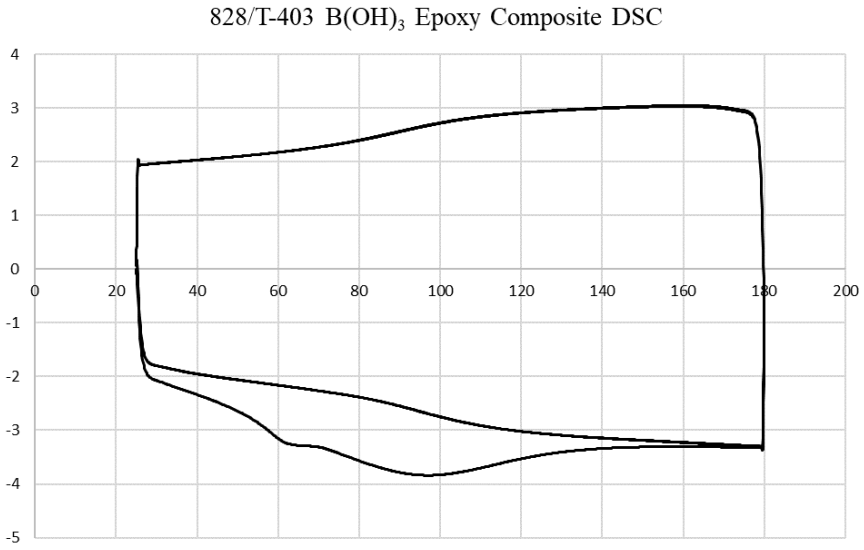


Figure 11. DSC thermogram of T-403:$B(OH)_3$ cured epoxy composites with a boric acid concentration of 10.0 vol%.

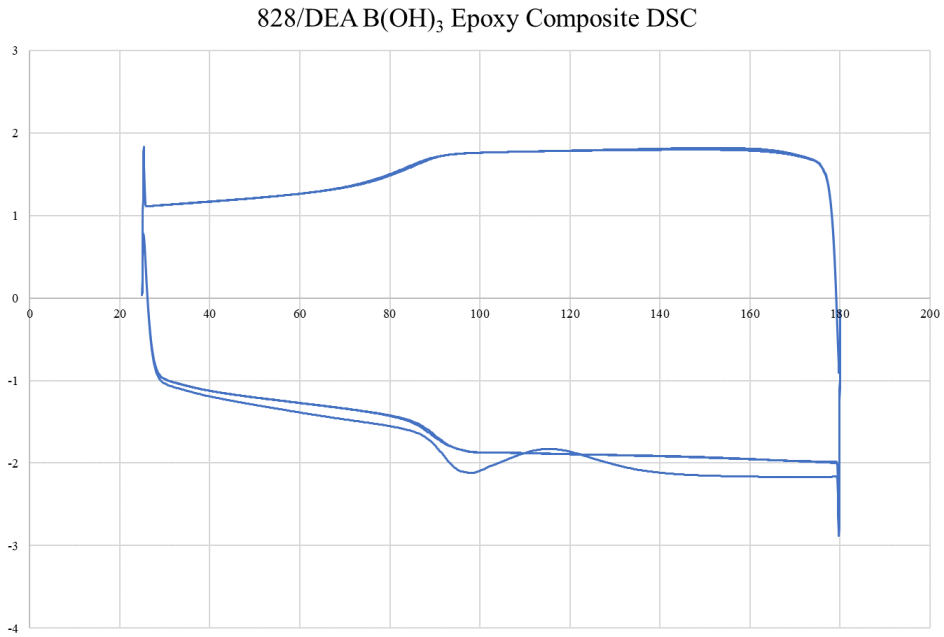


Figure 12. DSC thermogram of DEA:$B(OH)_3$ cured epoxy composites with a boric acid concentration of 10.0 vol%.

3.2 Epoxy Composites- Degradative Performance

Testing the degradative performance of the cured epoxy samples was performed via two methods. Under static conditions, cured epoxy samples were soaked for 6 weeks in either a pH 9.0 aqueous solvent or in denatured ethanol. Samples were removed weekly and monitored via microscopy to track the formation of any voids or surface erosion. After 6 weeks of total soak time, minimal differences were observed in all T-403 and DEA cured samples that were soaked in the pH 9.0 solution, indicating that the materials were relatively resistant towards caustic environments. This can be observed in Figure 13 and 14 below. In contrast, T-403 and DEA cured samples that were soaked in denatured ethanol showed considerable swelling and some light surface cracking, even within one week of soaking. Significantly, the extent of cracking and swelling was highest on the T-403 and DEA samples that had high (10 and 20 vol%) boric acid content; as boric acid concentration was reduced, the extent of swelling and cracking was also reduced. However, whether these changes were caused directly by the interaction of ethanol with the boric acid or some other mechanism was inconclusive.

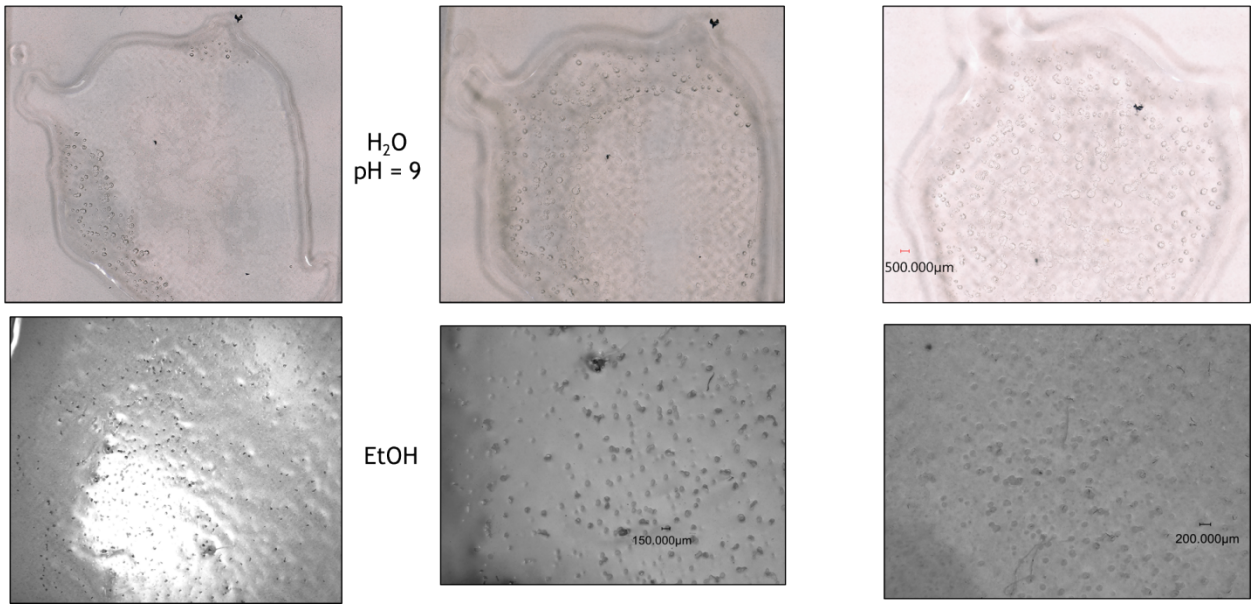


Figure 13. Optical images of epoxy composites cured with DEA-$B(OH)_3$ (20 vol%) after exposure to alkaline water and ethanol under static conditions.

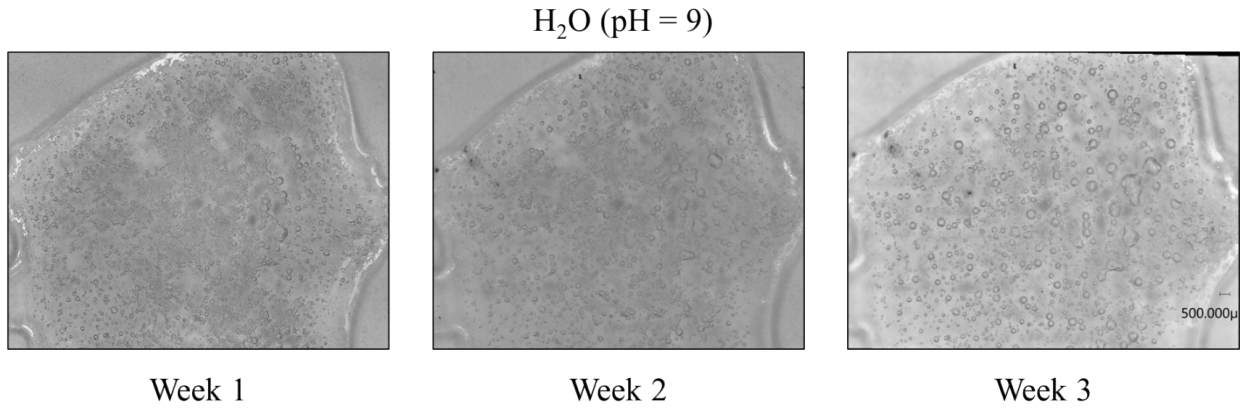


Figure 24. Optical images of epoxy composites cured with T-403 $B(OH)_3$ (20 vol%) after exposure to alkaline water under static conditions.

Another method used to test degradative performance was via Soxhlet extraction, which takes advantage of dynamic effects of refluxing solvent and the increased surface area of powdered epoxy samples. Soxhlet extractions were performed on epoxy systems cured with either T-403 or DEA (each containing 5 vol% boric acid), in the presence of refluxing ethanol. After refluxing for 72 hours, the resulting mass loss of the T-403 cured epoxy was measured to be ~17 mg, with no

recoverable material in the extractant. For the DEA cured epoxy, the mass of lost product was considerably higher at 231.5 mg, with no recoverable material in the extractant.

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 novel small synthesis and characterization, and the overall general R&D will briefly be given in a University of Arizona technical seminar funded through SNL recruiting. Furthermore, we hope to present the work at the 2022 Spring ACS National Meeting in San Diego, CA.

Each of the three amine-based boron compounds prepared in this project have follow on R&D that necessitates investigating. The DETA complex, if the structural hypothesis is proven to be correct, has potential in multiple application areas, such as in chemical sensing, surface modifications, and as a precursor to boron nitride (BN). The TGA presented in the results showed very high thermal stability in an inert atmosphere compared to the other amine compounds, and this may be a result of BN formation due to the distinct B-N bonds present in the precursor molecule and upon decomposition under N_2. Furthermore, the geometry of and functional groups (O-H and N-H) may be useful for bonding to surfaces that have -OH groups present, such as silica and alumina, for chemical modifications. An application relevant to the aforementioned use is in chemical separations and sensing, where hydrogen-bonding interactions play a key role.

The DEA complexes, though previously published, are the only ones in the set of three that still yield plausibility for the targeted application. The N-H present in DEA allows for curing into the epoxy network while the -OH groups allow for reversible bonding to boric acid. Based on qualitative observations on the hygroscopicity of the DEA solids, water is very easily absorbed onto the material, thus the hydrolysis reaction inside an epoxy remains possible. The other two amines, having exclusively amine functional groups and not alcohols, are not as likely to degrade based on the bonding mechanism, which does not seem to be the originally hypothesized coulombic-based acid/base reaction shown in the introduction.

The T-403/boric acid ^{1}H NMR results look to be either 1) a purified component of a stereochemical mixture, 2) a more symmetric mixture than the neat T-403 oligomer, or 3) a novel macrocycle compound. At the point of this report submission, we are unsure of exactly what is chemically happening to account for this observation; however, if boric acid is aiding in either 1) the isolation of specific diastereomers or 2) increasing symmetry of this structurally-complex chiral oligomer, a truly novel use of the very cheap boric acid has been found.

NNSA and DOE's diverse mission areas would find usefulness in the multiple material novelties described above. To reiterate, this includes the preparation of BN, a highly versatile and stable material, and novel small molecules that may be used to produce a monolayer of BN or to chemically modify a substrate in general, such as for chemical separations/sensing purposes. Boron-containing materials also hold interest in neutron attenuation or sensing applications, which ties to many of DOE/NNSA's mission areas.

CONCLUSIONS

Boric acid was mixed neat with three amine compounds (DEA, T-403, DETA) to form complexes (some novel) that, when cured with EPON 828 epoxy resin, was intended to yield epoxies with removable borate ions with exposure to neutral-to-basic water. This chemistry was based on previous SNL work that used N,N-dyglycidal-4-glycidaloxyaniline and the acidic triprotic phosphotungstic (PTA) acid to form a columbic complex that dispersed the PTA in the neat epoxy resin. Borate ion incorporation into cured epoxies would allow a removable component in the material system, yielding high porosity and thus high surface area, which would increase its degradation rate in the environment.

DEA and T-403 mixtures yielded clear, colorless mixtures, and DETA samples yielded a white precipitate. Trituration of the DEA and T-403 liquid mixtures also yielded white solids. Characterization of these mixtures/solids revealed 1) the DEA complexes to be a mixture of previously published borate esters and the Lewis acid-base adduct of the two reactants, 2) the T-403 complex to be a single isolated set of diastereomers from the neat T-403 mixture, and 3) the DETA complex to be a single molecular species that can be recrystallized and has high thermal stability. All solids were found to be very hygroscopic and readily soluble in polar protic solvents.

Epoxy samples were prepared with the DEA and T-403 mixtures since they remained in liquid form upon boric acid dissolution. The epoxy composites prepared with the DEA mixtures exhibited complete curing and no void formation, indicating complete mixing of the components and the absence of unreacted or off-gassing species. For the epoxy composites obtained from the T-403 mixtures, samples ranged from partially cured to fully cured, and significant void formation was observed throughout the samples.

The degradative performance of the cured epoxy samples was tested under static conditions (solvent soaking) and dynamic conditions (Soxhlet extraction). Under static conditions, cured epoxy samples were soaked for 6 weeks in either a pH 9.0 aqueous solvent or in denatured ethanol. Weekly analysis via microscopy showed little change in aqueous-aged samples, while samples aged in organic media showed considerable swelling and surface cracking, the causes of which were inconclusive. In contrast, Soxhlet extractions (refluxing ethanol, 72 h) resulted in minimal

sample loss (~17 mg) on T-403 formulated epoxies (boric acid = 5 vol%); for DEA cured epoxies (boric acid = 5 vol%), the mass of loss product was considerably higher at 231.5 mg.

REFERENCES

1. Chamas, A.; Moon, H.; Zheng, J.; Qiu, Y.; Tabassum, T.; Jang, J. H.; Abu-Omar, M.; Scott, S. L.; Suh, S., Degradation Rates of Plastics in the Environment. *ACS Sustainable Chemistry & Engineering* **2020,** *8* (9), 3494-3511.

2. Anderson, B. J., Cationic cure kinetics of a polyoxometalate loaded epoxy nanocomposite. *Journal of Polymer Science Part A: Polymer Chemistry* **2012,** *50* (21), 4507-4515.

3. Leventis, N.; Sotiriou-Leventis, C.; Saeed, A. M.; Donthula, S.; Majedi Far, H.; Rewatkar, P. M.; Kaiser, H.; Robertson, J. D.; Lu, H.; Churu, G., Nanoporous Polyurea from a Triisocyanate and Boric Acid: A Paradigm of a General Reaction Pathway for Isocyanates and Mineral Acids. *Chemistry of Materials* **2015,** *28* (1), 67-78.

4. Zarzyka, I., The Modification of Polyurethane Foams Using New Boroorganic Polyols: Obtaining of Polyols with the Use of Hydroxypropyl Urea Derivatives. *International Journal of Polymer Science* **2014,** *2014*, 1-9.

5. Myers, R. E.; Dickens, E. D.; Licursi, E.; Evans, R. E., Ammonium Pentaborate: an Intumescent Flame Retardant for Thermoplastic Polyurethanes. *Journal of Fire Sciences* **1985,** *3* (6), 432-449.

6. Ito, Y.; Aoki, D.; Otsuka, H., Functionalization of amine-cured epoxy resins by boronic acids based on dynamic dioxazaborocane formation. *Polymer Chemistry* **2020,** *11* (33), 5356-5364.

7. Stepina, I., Creating an effective wood protectors from boric acid and aminoalcohols. *IOP Conference Series: Earth and Environmental Science* **2019,** *403*.

8. Lappert, M. F., Organic Compounds Of Boron. *Chemical Reviews* **1956,** *56* (5), 959-1064.

9. Bellamy, L. J.; Gerrard, W.; Lappert, M. F.; Williams, R. L., 481. Infrared spectra of boron compounds. *Journal of the Chemical Society (Resumed)* **1958,** (0), 2412-2415.

10. Servoss, R. R.; Clark, H. M., Vibrational Spectra of Normal and Isotopically Labeled Boric Acid. *The Journal of Chemical Physics* **1957,** *26* (5), 1175-1178.

11. Hornig, D. F.; Plumb, R. C., Vibrational Spectra of Molecules and Complex Ions in Crystals. IX. Boric Acid. *The Journal of Chemical Physics* **1957,** *26* (3), 637-641.

12. Vineyard, B. D.; Godt, H. C., A Study of the Reaction of Boric Acid with Amines: Hydroxyboroxin-Amine Salts. *Inorganic Chemistry* **1964,** *3* (8), 1144-1147.

13. Segal, L.; Eggerton, F. V., Infrared Spectra of Diethylenetriamine and 2-(2-Aminoethylamino)ethanol. *Applied Spectroscopy* **1961,** *15* (5), 148-150.

LABORATORY DIRECTED RESEARCH & DEVELOPMENT

WHERE INNOVATION BEGINS

ADDENDUM

2 PROJECT OVERVIEW

Project Overview

PROJECT SUMMARY:
New materials and technologies are needed that can be used to reduce greenhouse gas emissions and improve recyclability of materials and components used in energy systems. Thermoset materials, such as epoxies, are heavily used where harsh environments are present; however, their robust material properties also make them persist with very slow degradation over long periods of time.

Creating novel epoxy material systems with multifunctional use while providing more efficient degradation pathways is desirable.

IMPACT:
The success of the proposed work would yield a foundation of novel and very applicable R&D to be further explored and developed using non-hazardous materials.

Financial Performance at Year-End

Accomplishments & Plan

ACCOMPLISHMENTS:
- Novel boron species from neat mixing of amine compounds with boric acid. DETA forms a triazaborinic acid, DEA forms a dioxazabornic acid (previously prepared in literature), and T-403 forms a tris(boramidic acid) macromolecule (all hypotheses).
- The DETA-based triazaborinic acid looks to form something highly stable at high temperatures under N_2, perhaps boron nitride (BN).

UPCOMING ACTIVITIES:
- Confirm the structure/composition of the DETA-$B(OH)_3$ product.
- Pyrolyze DETA-$B(OH)_3$ product under N_2 and get PXRD on remaining powder (BN?).
- Correlate high $B(OH)_3$ concentrations in DEA and T-403 mixtures

Risks, Issues, and Opportunities

RISKS
- **If $B(OH)_3$-amine complex does not form, yielding no permanent dispersion for cure & material testing, then alternative amines will be used after evaluation of why complex did not form.**
- **If $B(OH)_3$-amine complex formation negatively affects curing process/material property performance, then concentration will be evaluated to alleviate negative effects.**

ISSUES: Acid-base reaction necessary for borate extraction not occurring. Other B-N or B-O chemistry is forming bonds.

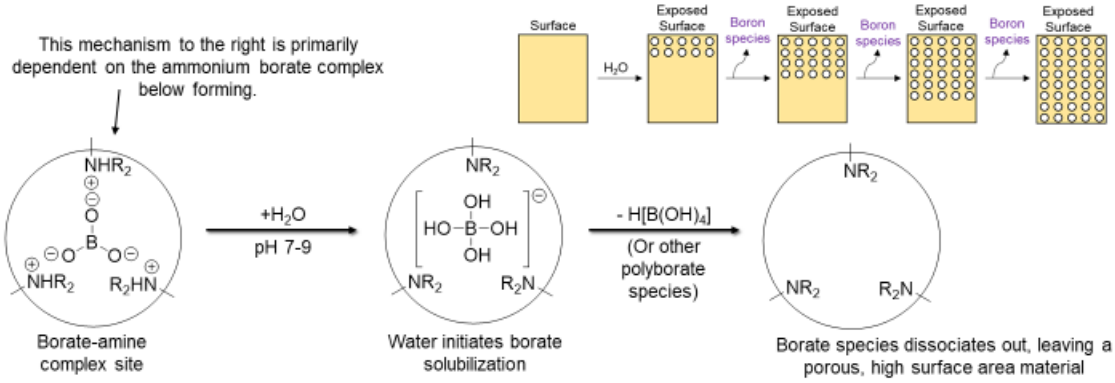
OPPORTUNITIES: Novel and cheaply made material combination for BN material preparation. Unique chemical structure of DETA-$B(OH)_3$ could yield benefits in other applications, such as chemical sensing.

LABORATORY DIRECTED
RESEARCH & DEVELOPMENT
WHERE INNOVATION BEGINS

3 MILESTONES & PROJECT HYPOTHESIS

Status of FY21 Project Milestones	Completion Date
Synthesis/Characterization of Amine Borates	09/21
Mixing/Curing/Characterizing of EPON 828 w/ Amine Borates	07/21
Water Degradation Studies	08/21
SAND Report	09/21

This mechanism to the right is primarily dependent on the ammonium borate complex below forming.

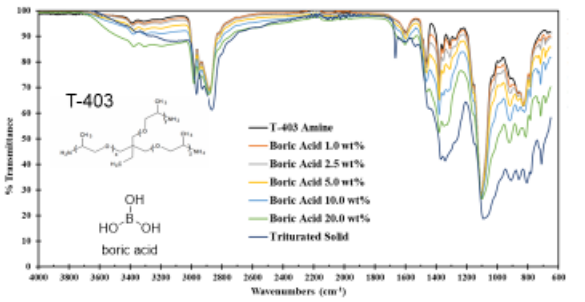


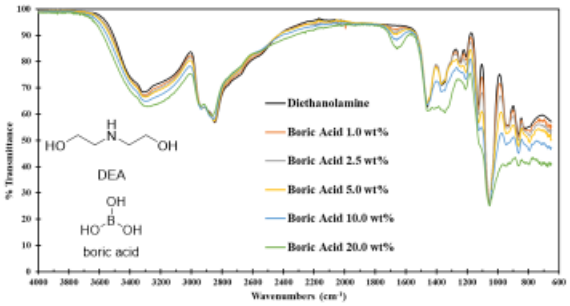
Borate-amine complex site

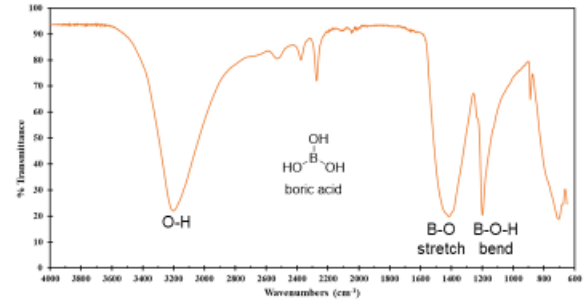
Water initiates borate solubilization

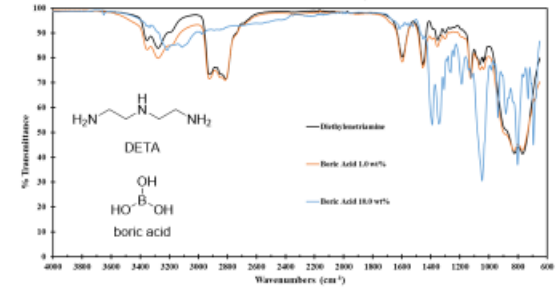
Borate species dissociates out, leaving a porous, high surface area material

4 FT-IR DATA FOR AMINE-$B(OH)_3$ MIXTURES



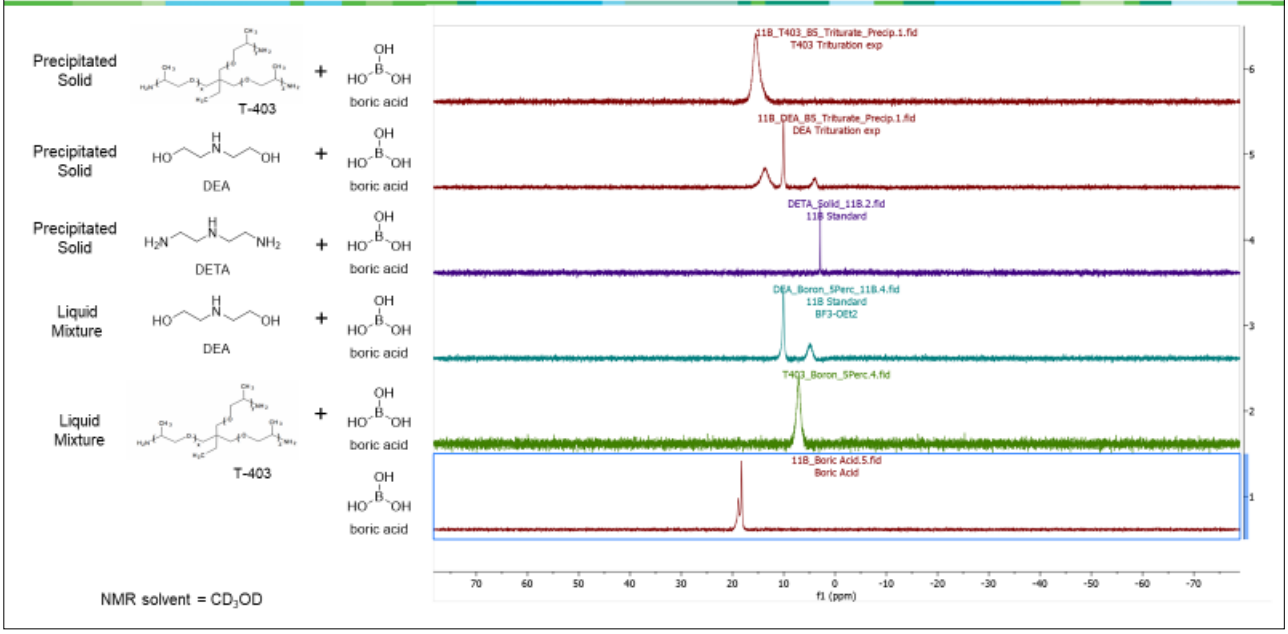






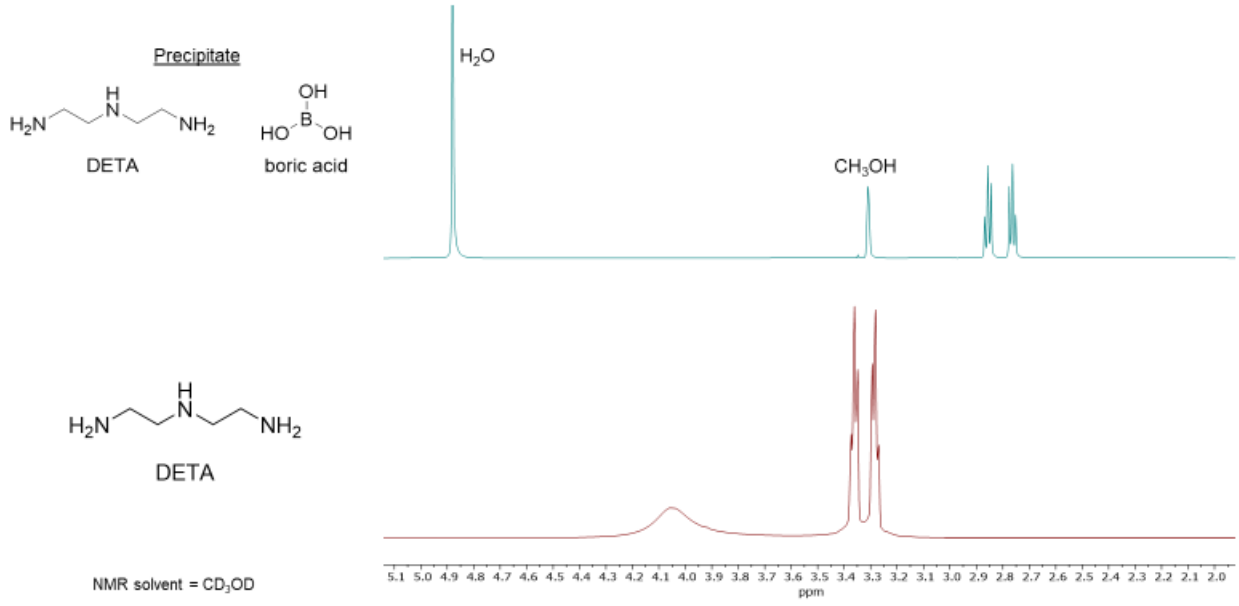
LABORATORY DIRECTED
RESEARCH & DEVELOPMENT
WHERE INNOVATION BEGINS

5 ^{11}B NMR DATA OF AMINE-B(OH)$_3$ RXN PRODUCTS



NMR solvent = CD_3OD

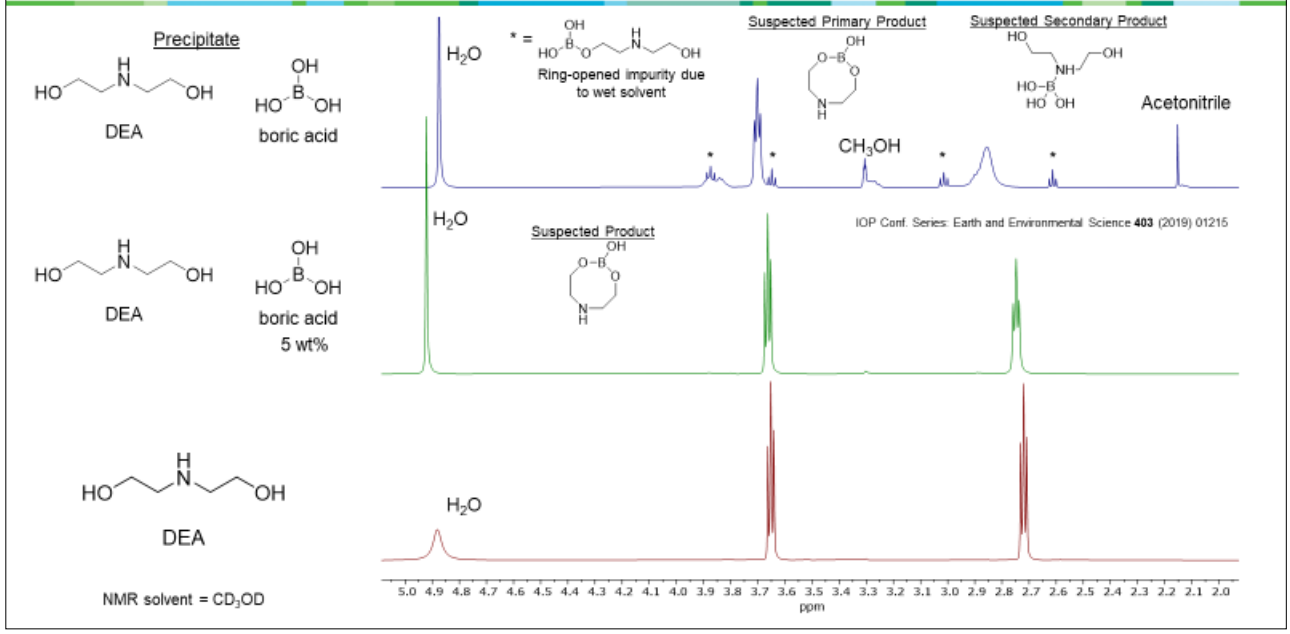
6 ^{1}H NMR DATA – DETA W/ B(OH)$_3$



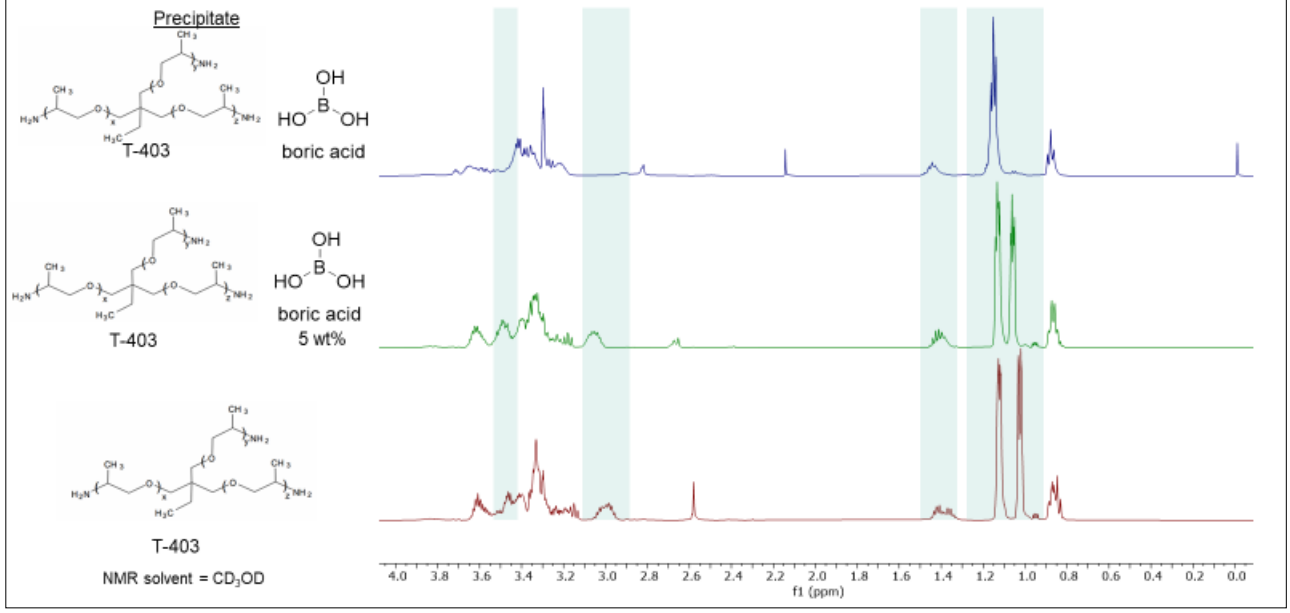
NMR solvent = CD_3OD

LABORATORY DIRECTED
RESEARCH & DEVELOPMENT
WHERE INNOVATION BEGINS

7 ^{1}H NMR DATA – DEA W/ $B(OH)_3$



8 ^{1}H NMR DATA – T403 W/ $B(OH)_3$



LABORATORY DIRECTED RESEARCH & DEVELOPMENT

WHERE INNOVATION BEGINS

9 UV-VIS DETERMINATION OF DETA-B(OH)$_3$ MOLECULAR WEIGHT

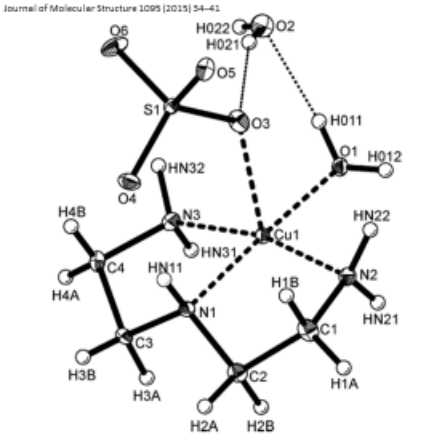
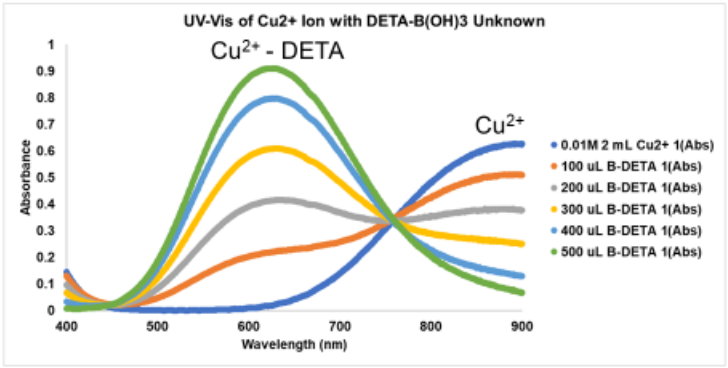


Fig. 3. Numbering system of the $[Cu(deta)H_2O]SO_4 \cdot H_2O$ discrete unit in **1**. Thermal ellipsoids are shown with the 50% probability level for non-hydrogen atoms.

Since at least one of the Ns from DETA are chemically involved with the B, 2 equivalents of DETA-B are most likely possible.



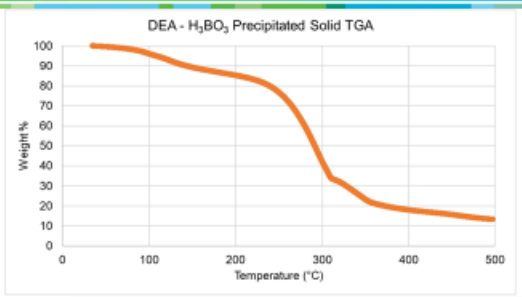
600 µL had lower absorbance, indicating no further reaction and dilution

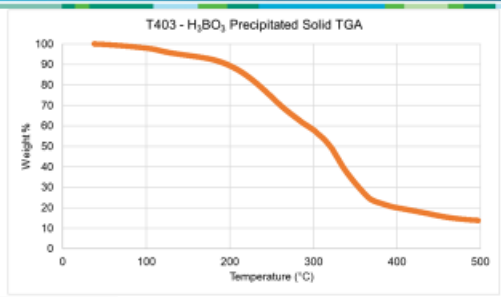
2 mL of 0.01 M Cu^{2+} = 0.02 mmol Cu^{2+}

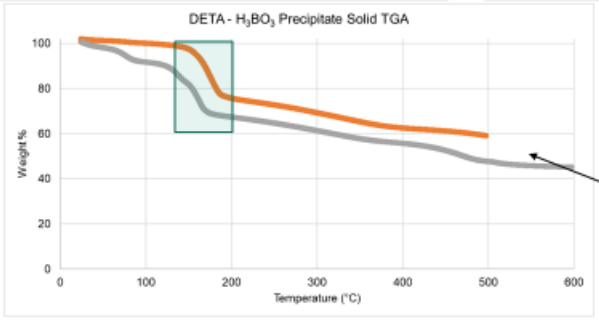
500-550 uL of 10 mg/mL unknown = 5-5.5 mg unknown

$$\frac{\text{5-5.5 mg}}{\text{0.04 mmol}} = \text{125-137 g/mol MW for unknown}$$

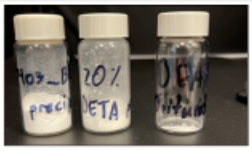
10 SYNTHESIZED AMINE-B(OH)$_3$ COMPOUND TGA DATA







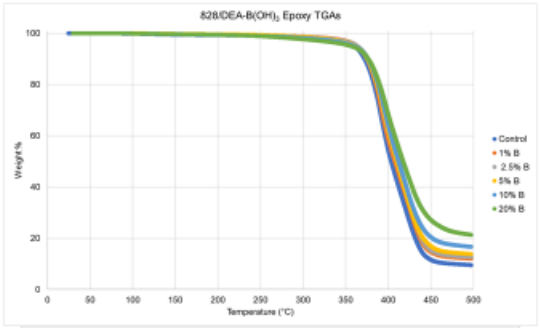
Have crystals now, will attempt to get structure through SC-XRD.

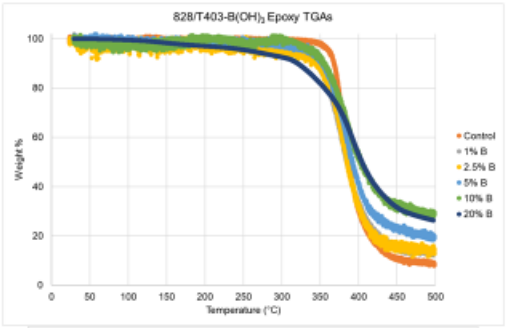


Very high weight % remains between 500 – 600 °C.

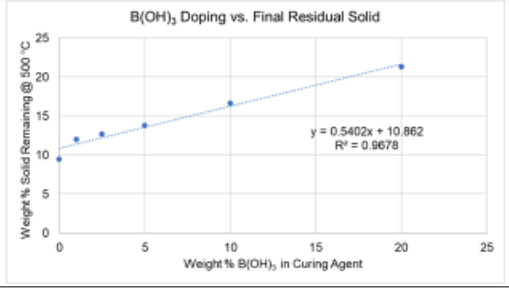
LABORATORY DIRECTED
RESEARCH & DEVELOPMENT
WHERE INNOVATION BEGINS

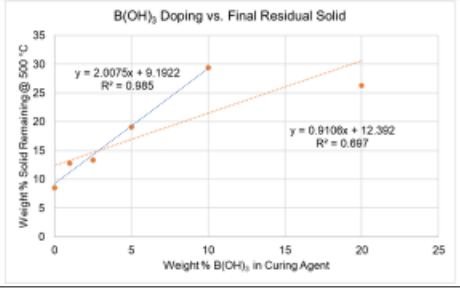
11 AMINE-$B(OH)_3$ EPOXY TGA DATA



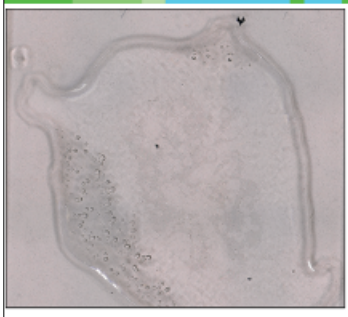


20% B potentially bad sample?

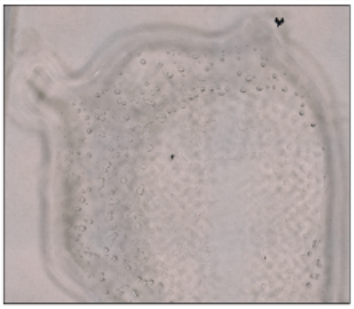


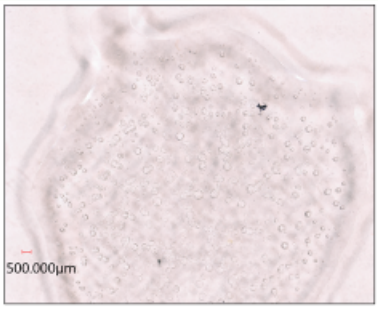


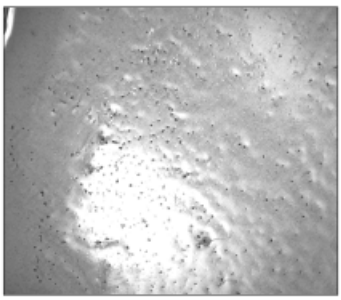
12 OPTICAL IMAGES OF WATER-EXPOSED 20% $B(OH)_3$ DEA EPOXIES



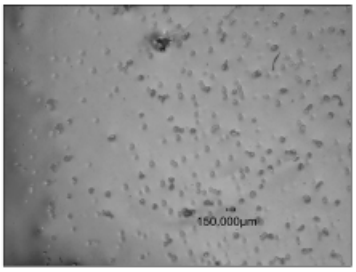
H_2O
pH = 9

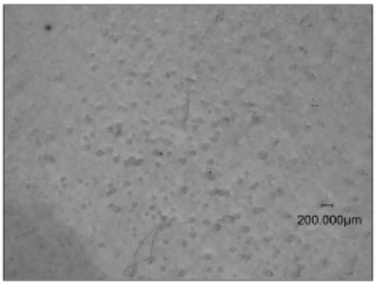






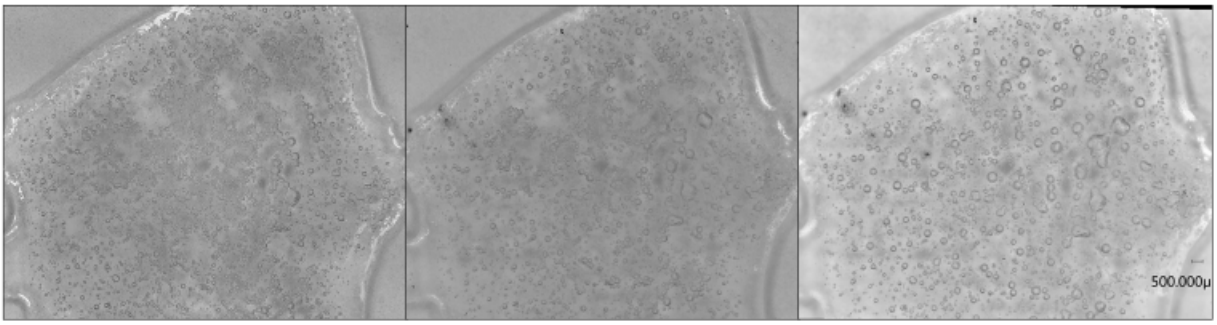
EtOH





13 OPTICAL IMAGES OF WATER-EXPOSED 20% $B(OH)_3$ T-403 EPOXIES

H_2O
pH = 9



1 week | 2 weeks | 3 weeks