TANNIC ACID: A KEY TO REDUCING ENVIRONMENTAL IMPACTS OF EPOXY

by

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Dedicated to the Flaming Triangle and my Mom.
They are my true inspiration.

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LIST OF ABBREVIATIONS

Tannic Acid	TA
Diglycidylether of bisphenol A	DGEBA or BADGE
Triethylene Tetramine	TETA
Brominated Rlame Retardant	BFR
Flame Retardant	FR
Fourier transform infrared Spectroscopy	FTIR
Thermogravimetric Analysis	TGA
Differential Scanning Calorimetry	DSC
Dynamic Mechanical Analysis	DMA

ABSTRACT

Epoxy thermosets have revolutionized the coating, adhesive, and composite industries but the chemicals from which they are synthesized have significant effects on the environment and human health not only pre-cure but also after crosslinking has occurred. Many flame retardants (FR), hardeners, and other additives used in epoxy thermosets are synthesized from petroleum-based monomers leading to significant environmental impacts at the industrial scale. Various bio-based modifiers have been developed to circumvent these environmental concerns; however, dispersing biologically-based molecules into the system without tradeoffs with other properties, especially mechanical properties and the glass transition temperature, has proven challenging. Tannic acid (TA) is a bio-based high molecular weight organic (HMWO), aromatic molecule. Although biologically sourced, TA is a pollutant in industrial wastewater streams, and there is desire to find applications in which to downcycle this molecule after extraction from these streams. The unique properties that make TA applicable in a variety of applications including leather tanning, burn wound treatment, and water purification are desirable in epoxy thermosets. In this study, we propose TA as an alternative additive for epoxy. We will uncover the usefulness of TA as an epoxy hardener and as a FR additive. Previous work uncovered that TA could be dispersed in epoxy with weights up to 37 wt%, the highest loading level achieved in literature for this molecule. Using TA as an epoxy hardener resulted in materials that had glass transition temperatures at and above 200ºC. Using TA as a FR additive resulted in intumescent-behavior previously unseen with TA in epoxy. Chemical functionalization with acetic anhydride further enhanced the behavior resulting in a reduction of the peak heat release rate of the materials by 80%. Ongoing research in the use of solvent, metal ion complexation, and water-borne epoxy containing TA will additionally be explored. The result of this work indicated that TA showed significant promise as a biologically-based functional additive as a flame retardant and epoxy hardener and could reduce environmental impact of many currently available products.

1. INTRODUCTION

Portions of this work are based on work that was published in *Journal of Polymer Science Part A* and has been submitted for review in *Green Materials.* This chapter is reproduced from these sources with permission. This chapter is entirely my own work as a method of introducing the audience to the work within the document.

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1.1 Background Information

In 2015 global plastics demand exceeded 300 million tons, and this value has been growing steadily ever since.[1, 2] Since 1980, the plastics industry has grown at an annual, average rate of 3.4 percent, with US plastics companies alone employing over 1 million workers and providing nearly $379 billion in annual shipments.[1, 2] Plastics are used in a variety of applications due to their low density, the ease with which they are processed, and their low cost.[3] Two major drawbacks to their prevalence are that the source for most commercial plastics is petroleum and 40% of the total consumption of plastics is single or short-term use.[1-3] In tandem, this means that producers are using non-renewable resources to make a product that will be used once or twice and then put into waste. Most plastics products are non-compostable and non-biodegradable and thus end up persisting in the waste streams, like landfills. Rapid, often unplanned, urbanization can often leave municipalities overwhelmed and unprepared for the disposal of increasing amounts of waste (Figure 1.1).[3] Further, separation of the constituent chemicals of plastics is often quite challenging, exceedingly expensive, and can require a significant amount of energy; thus, there is little drive to recycle these products industrially.[1, 2] Therefore, when considering sustainability, one of the most commonly targeted materials is plastics.[1-3]

Figure 1.1: A main thoroughfare in Jaipur, Rajasthan, India in which an overwhelmed central waste system leaves single-use plastic and other waste on the side of the road.

Polymers can be designed to have properties desirable to a multitude of applications. Thermoplastic polymers, such as nylon, polyethylene, or polyvinyl chloride, are found in applications such as piping, food packaging, insulation, and clothing.[4] Thermoset polymers, such as epoxies and polyurethanes, are often found in coatings, structural applications, and adhesives.[5-7] There has been a significant amount of research to increase the sustainability of thermoplastic polymers, in particular, with regard to food packaging applications which currently demand the largest market share of the plastics industry.[1, 2] Researchers have found ways to sustainably source a variety of thermoplastics including polyhydroxyalkanoate,[8-12] polylactic acid,[12, 13] poly(butylene succinate),[14, 15] poly(trimethylene terephthalate),[12, 13, 16] polyethylene,[13, 17, 18] polypropylene,[12, 19-21] polyethylene terephthalate,[12, 22, 23] and others.[12] There has even been a significant amount of work in the area of thermoplastic elastomers including triblock copolymers consisting of bio-derived poly(lactide) sourced from corn and sugar beets reacted with a variety of end groups including poly(menthide) synthesized from (-)-menthol found in mint leaves, as well as bio-sourced poly(ethylene glycol), poly(isoprene), and poly(ricinoleic acid).[24-29]

There is also a significant amount of research on the development of sustainable thermoset polymers; in particular, with regard to the adhesives and coatings industries. Previous researchers have developed sustainably-sourced acrylics using acrylic acid and methacrylic acid soured from biomass.[30, 31] Renewable, unsaturated polyester thermosets have also been synthesized using 1,2-propylene glycol sourced from triglycerides and sugars.[32-34] Bio-inspired urethanes have been synthesized including bio-sourced hexamethylene diisocyanate and isophoronediisocyanate.[35-38] Some of the above chemical synthesis pathways have been patented and used industrially for the preparation of thermoset polymers that are biologically derived. However, while there is also a significant amount of work being done in the area of epoxy thermoset sustainability, there are very few industrially-viable biologically-sourced epoxy monomers currently used.

Due to their excellent mechanical strength, good thermal, electrical, and chemical resistance and superb adhesion to many substrates, epoxy based polymers are considered one of the most versatile and important thermosetting polymers.[39, 40] Epoxy polymers are used in a wide range of applications including coatings,[41] adhesives,[42] structural composites,[43] insulating materials,[44] and in components of electronics.[5, 6] Global epoxy market demand is expected to increase at a compound annual growth rate of 7.9% from 2016 to 2020, with an expected annual demand of 2,115.6 ktons in the coatings sector alone by 2024.[7, 45, 46]

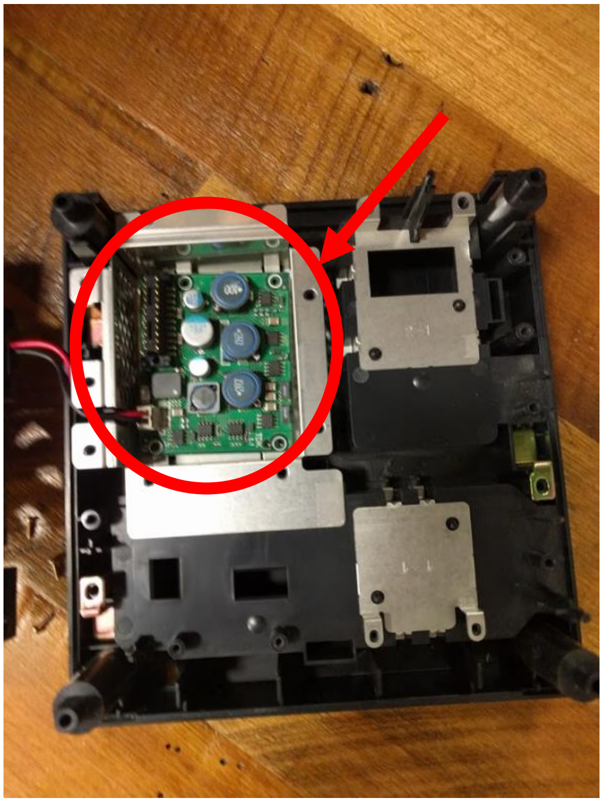

Figure 1.2: An epoxy circuit board in a dismantled electronic device.

An epoxy thermoset is often made of two constituent chemicals: an epoxy resin and a hardening agent, which react to form a molecular-level, dense, covalent chemical network. For many applications of epoxy polymers, the material is subject to high-temperature environments after the initial crosslinking procedure. Because of this, not only do these materials need to be stable in high-temperature environments but they also need to maintain their stiffness at higher temperature. Currently, after initial synthesis, several electronic components are soldered to epoxy circuit boards at temperatures close to 180°C although their glass transition temperatures (T_g) tend to be closer to 140°C.[6] Repeatedly exposing these epoxy thermosets to temperatures significantly above their T_gs leads to a localized softening of the thermoset during the soldering process. This behavior not only greatly hinders the process overall but also leads to reduced T_g and temperature of thermal decomposition (T_d) of the bulk material.[47] Because of this reduction in thermal stability and thermomechanical properties, the T_g and T_d are often used when determining the application in which an epoxy material can be used. Epoxy materials with T_gs above 160 ºC are considered high

T_g epoxy materials in industry.[48, 49] Enhancing both T_g and T_d can greatly increase the variety and diversity of applications in which epoxy materials can be utilized.

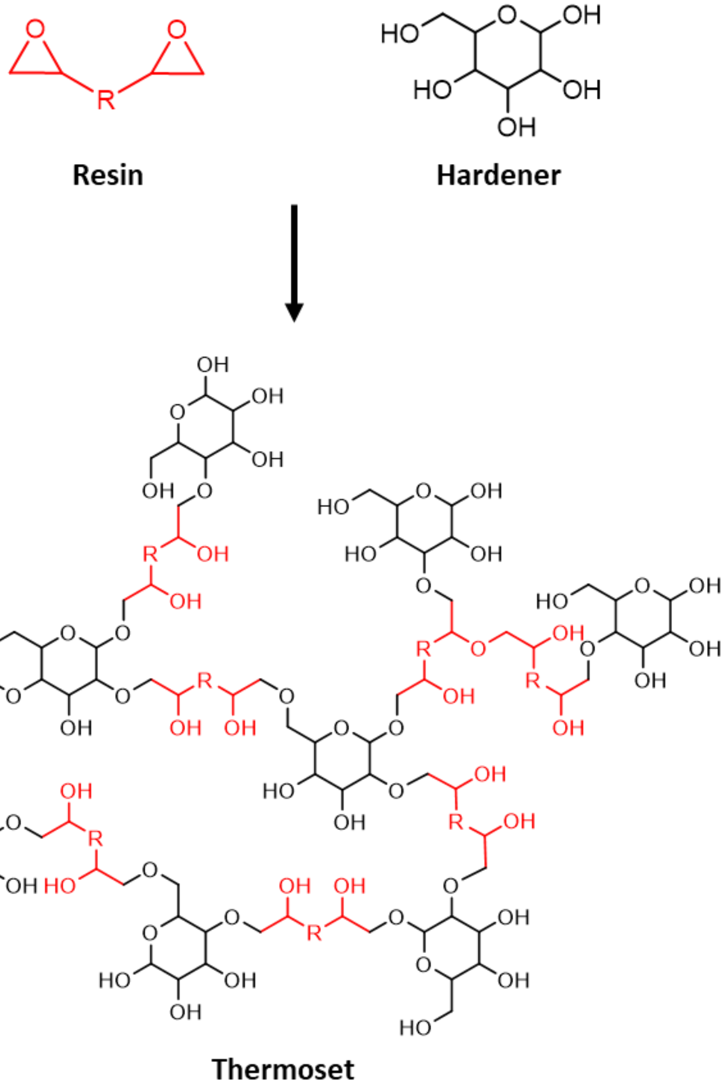

Figure 1.3: Epoxy thermoset synthesis pathway (note: synthesis is 3-dimensional and is simplified for this visualization).

While the properties of epoxy thermosets are desirable there are many concerns with their use in application. Firstly, the precursor chemicals and many epoxy additives are industrially synthesized from non-renewable petroleum resources which raises concerns with the long-term viability of this material to be industrially available to the scale at which it is currently utilized.[40, 50] To combat this, many researchers have striven to develop biologically-sourced monomers.[51] A second major concern with epoxy thermosets is that while they can form a thermally-stable char in the event of a fire in some applications, because of the high temperature demand in many applications and processing epoxy can actually be flammable.[52, 53] To combat this, flame retardant additives are almost always added to the materials and are often mandated legislatively.[53] A third major concern with the use of epoxy is the toxicity of the precursor chemicals and flame retardants is well known, especially for hardeners used in high temperature applications.[54, 55] Even for cured epoxy resins, toxicity cannot be avoided because of the possibility of incomplete consumption of curing agents and the subsequent hazards introduced by the residue.[40]

Despite the known health and environmental impacts of all commercially available curing agents of epoxy resins, such as the diglycidyl ether of bisphenol A (DGEBA), polyamines,[56, 57] acid anhydrides,[40, 57] and sulfur-based hardeners,[58] there are currently very few non-toxic resins and no non-toxic curing agents that are used industrially.[40] Additionally, although the toxicity of flame retardants utilized industrially for epoxy products is well known - including halogenated flame retardants such as tetrabromobisphenol A (TBBPA) and polyphosphorylated compounds such as triphenyl phosphate (TPP) – which are found to have high persistence, bioaccumulation, and toxicity and have been linked to a variety of health impacts including decreased baby size and cancer – their flame retardant functionality remains unmatched and they continue to be used in epoxy in a variety of applications, including printed circuit boards (PCBs).

In order to combat concerns with toxicity and avoiding petroleum as a source for epoxy precursor units and flame retardant additives, researchers have been looking for renewably-sourced alternatives which are traditionally sourced from plants. Biologically-sourced, non-toxic compounds could alleviate the toxicity and renewability concerns simultaneously. To replace the epoxy resin phase, many have looked at epoxidized natural oils,[59, 60] isosorbides,[61] furans,[62] phenols and polyphenols,[63] natural rubber,[64] lignin,[65] and rosins.[66, 67] To replace the epoxy hardener, researchers have functionalized grapeseed, cardanol, and furans with reactive amine groups,[68-71] anhydride-functionalized terpene,[72] and used un-modified compounds like cardanol, amino acids, citric acid and other acids, and rosins.[69, 73-76] Additionally, biologically-sourced flame retardants have been explored such as cellulose[11], deoxyribonucleic acid[12], lignins[13], condensed tannins and tannic acid (TA).[14] However, the use of biologically-sourced compounds in this application has many limitations including most notably the fact that many biologically-sourced additives for epoxy are not compatible enough in epoxy to meet the intense material demands including mechanical and thermomechanical properties and flame retardancy.

There are several methods that have been used to circumvent this compatibility challenge for biologically-sourced additives. Surfactant can be used to assist dispersion and increase the overall dispersion of the additive[15,16], but excess surfactant can effect the resulting thermomechanical properties such a T_g – which are of vital importance for epoxy which is often used or processed at high temperature. Using solvent has been found to greatly increase dispersion of these additives in polymers,[17] but will also lead to the environmental emission of volatile organic compounds and reduce the mechanical properties of the resulting thermoset. Chemically modifying the additive to better match the system into which it is being inserted can increase the interfacial compatibility of the additive and the polymer matrix[18] but can potentially make the product more difficult to commercialize due to the added chemical steps in manufacturing. An additional concern with this method is that many of the reactants are synthesized from petroleum, which is a non-renewable resource, and the synthesis pathways can involve toxic compounds. Impregnation of the additive is another method for increasing dispersion of these particles[19], but it requires a large scale and optimized lyophilization process to preserve shape integrity[20]. Due to these concerns, the commercializability of biologically-sourced additives into polymer matrices is dependent on the minimization of the complexity of the polymer dispersion processing mechanism.

There is a need for exploration of these and many other processing mechanisms to enable the dispersion of such biologically-sourced molecules into hydrophobic polymer systems. However, there is very limited research in this topic for several bio-based chemicals above.

1.2 Tannic Acid Background

Polyphenolic molecules are molecules that contain numerous phenol structural units. These phenol groups help determine their unique physical and chemical properties. Some examples of naturally occurring polyphenolic molecules include lignins, flavonoids, quinones, and tannins.[77] Tannins are distinguished from the others in this list because of their unique ability to complex with biomolecules.[77] Up to Fifty percent of the dry weight of leaves comes from condensed tannins, and condensed tannins make up the majority of all naturally occurring polyphenols.[78] Additionally, principal human dietary sources of tannins are tea and coffee,[79] with other major sources including wines aged in oak barrels,[80] berries such as strawberries, cranberries, raspberries,[81] and beer.[82]

There are three main types of naturally occurring tannins. They are hydrolysable tannins (HTs), condensed tannins (CTs), and phlorotannins (PTs).[83] The three main types of hydrolysable tannins are gallotannins (GTs), ellagitannins (ETs), and complex hydrolysable tannins (CHTs).[77] The simplest hydrolysable tannins are GTs. GTs are esters of gallic acid and an aliphatic polyol. The polyol is almost exclusively D-glucose, but can vary.[83] Attached to the D-glucose molecule are 4 phenol groups at the C2, C3, and C4 sites and 1 hydroxyl group at the C6 site, and are available for gallic acid linkage. The simplest fully-substituted HT is formed when all phenol and hydroxyl groups are substituted with gallic acid.[83] However, after full substitution takes place, additional self-esterification between gallic acid subunits can take place leading to depsidic linkages, and a wide variety of chemical product possibilities.[84] Finally, tannic acid (TA) is formed after two gallic acid units have been added to each phenol group on the molecule (Figure 1.4). Please note that the chemical formula for TA is usually given as $C_{76}H_{52}O_{46}$ but it often contains a mixture of related compounds based mainly on the glucose ester of gallic acid.

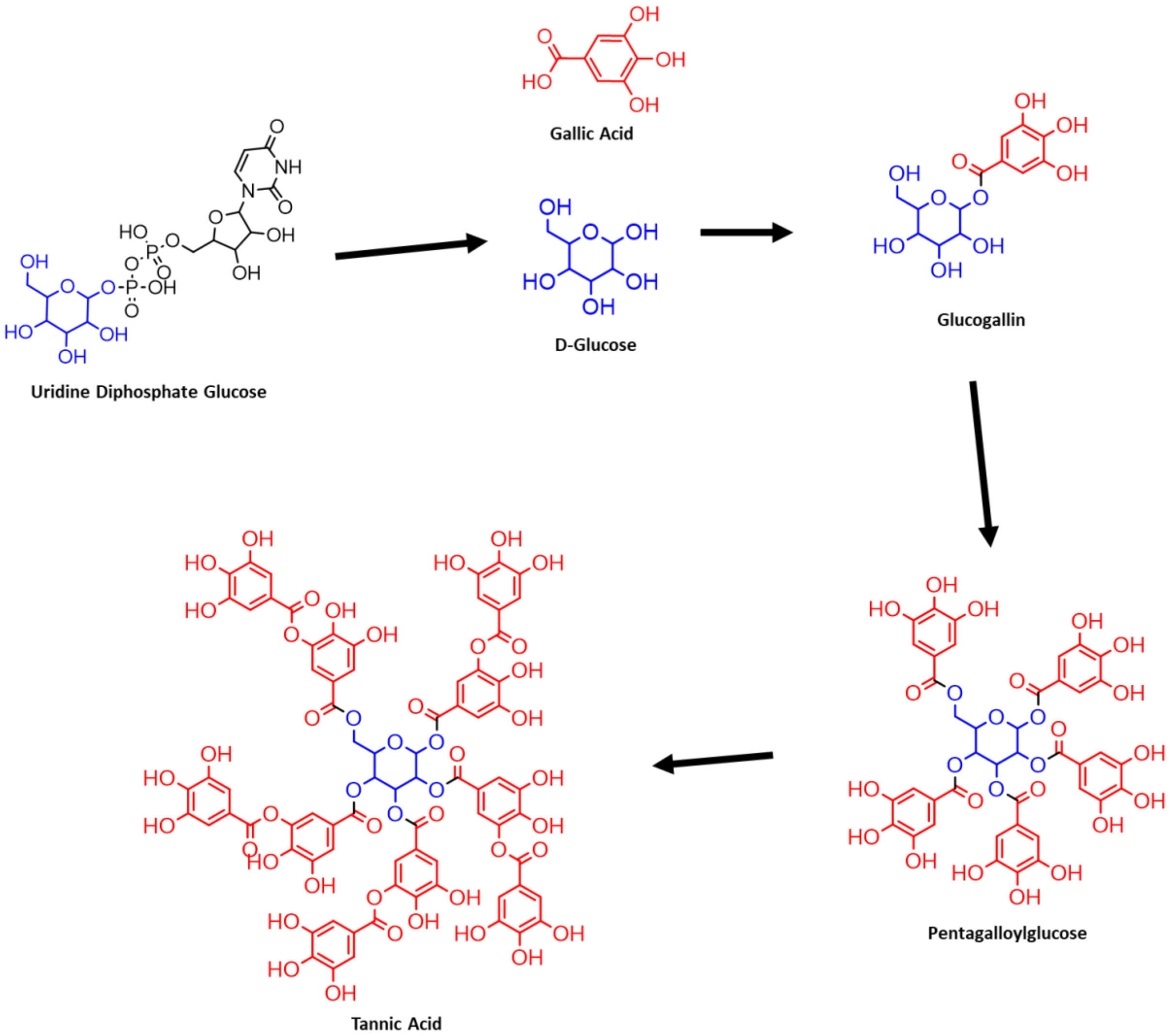

Figure 1.4: Synthesis pathway of tannic acid (TA) in nature. Note that TA's structure is not exactly as shown in every case and the actual structure of TA is dependent on the number of gallic acids and specific -OH bonding site on the gallic acid.

TA has two unique properties that make it desirable in a wide variety of industrial applications. First, its chemical heterogeneity allows it to strongly coordinate with proteins in solution, which is key to the defensive mechanisms of many plants.[85] This discovery led researchers to consider that it might be successful in a wide variety of biomedical applications including treatment for burn wounds, poisoning, and cancer. However, though TA shows promise in these applications, gallic acid, the monomer unit of the TA structure, has been found to be hepatotoxic in high amounts and limits its applicability in biomedical applications.[86] Second, TA can coordinate with metallic ions in solution resulting in metal-TA nanoparticles which can be dispersed in a variety of materials. This discovery had led to innovation in the area of enhanced MRI imaging, water filtration, and functional coatings that are anticorrosive and antifouling.[87, 88] However, the research and innovation in this space has only just begun and much is yet to discovered. Thirdly, TA's plethora of phenolic -OH groups (more correctly known as galloyl groups) are quite good at scavenging radical electrons from solution in plants to help eliminate reactive oxygen species (ROS), reactive nitrogen species (RNS), and reactive sulfur species (RSS) that would otherwise harm the plant.[89] It also has the ability to crosslink into chemical networks at elevated temperatures which increases char formation, allowing trees, like Redwoods, to survive forest fires for hundreds of years.[90]

This and other work has led researchers to consider using TA as a biologically-sourced additive in polymer systems. Adding TA to polymers does improve their flame retardancy,[91, 92] but not significantly enough to compare with commercially available products with which it would need to compete. The primary explanation for this behavior is TA's chemical heterogeneity lowers its solubility in more hydrophobic polymer systems.[93] As a result, there is a limitation to how much TA can be added to polymers to improve thermal properties and flame retardancy without significantly affecting other properties. Low loading levels of TA result in enhanced properties that seem promising, but past compatibility limitations the resulting polymers just do not meet the need required by the applications – most notably the thermal and thermomechanical properties as well as the flame retardancy.

In order to combat the compatibility limitation on the flame retardancy, researchers have performed chemical functionalization to better match TA to hydrophobic polymer systems. Previous work identified that surface modification of TA using epoxy resin could increase the compatibility of the molecule; however, the dispersion of up to 8 wt% TA by this method did not increase the flame retardancy of the composite significantly.[26] Additionally, others have used this same chemical reaction between TA and epoxy rings to functionalize the molecule with hydrophobic carbon chains to enhance dispersion, but again flame retardancy was limited.[27] Other researchers have used trans esterified the molecule to increase its hydrophobicity and flame retardancy in nylon and PLA systems.[28] Even slight degrees of modification of the molecule showed drastic changes in solubility, as slightly-modified molecules were no longer soluble in water. Varying the degree of functionalization from low to high-esterification showed very little change in the compatibility output. This being said, researchers showed that acetylation of TA increased its flame retardancy in nylon and PLA, but no researchers have studied how acetylation of TA affected its flame retardancy in epoxy thermosets. However, acetylation of the molecule using acetic anhydride could additionally affect the ecotoxicity of the resulting additive. This is for two reasons: 1) the reaction to creating acetylated tannic acid has previously proven quite wasteful with low reaction yields and 2) industrial synthesis methods for preparation of acetic anhydride involve sourcing from petroleum and the use of many toxic compounds for isolation.

Additionally, the galloyl -OH groups on the TA molecule have been found previously in the literature to react with epoxy rings, though not for the above described applications.[94] Previous researchers have used this method to increase the dispersion of TA in epoxy systems by using short carbon chains that are mono-functionalized with oxirane.[95, 96] The result showed promise as a functional additive in epoxy and did better match the solubility of the polymer system. Other researchers have looked at this chemical reaction as a method for covalently attaching TA to a polymer backbone for many desirable applications including water filtration. This chemical reaction could prove useful because TA could be utilized as a biologically-sourced phenolic epoxy hardening agent. The high phenol density (25 OH/TA) of the molecule indicates that it could potentially form a highly-dense crosslinking network resulting in high thermal and thermomechanical properties. Additionally, if one could utilize this reaction using multi-functional epoxy, one could potentially form a biologically-based epoxy resin system with additional flame retardant functionality. Previous researchers have looked at TA as a biologically-sourced epoxy hardening agent in biologically-sourced epoxy resin, but the resulting properties they obtained were too low for industrial applications.[97] Additionally, previous researchers have utilized surface-functionalized TA as a biologically-based epoxy resin but explored biologically-sourced epoxy surface modifiers which resulted in properties that could not meet material demands industrially.[98] However, no previous literature has studied the use of TA as a biologically-sourced epoxy hardening agent for currently available epoxy resins, such as DGEBA. Additionally, no one has surface-functionalized TA with epoxy resin to result in a biologically-based epoxy resin. The main reason for this is that DGEBA, and the bisphenol A (BPA) molecule from which is it synthesized, have known toxicities as previously discussed. However, to get a better understanding of the feasibility of TA as a hardening agent and resin requires thermal properties which are currently unmatched by biologically-sourced epoxy resins and hardeners.

1.3 Motivation and Problem Statement

The primary purpose of this dissertation is to introduce the many avenues in which TA can be dispersed into epoxy matrices to enhance the sustainability of the system. This document aims to answer the following questions: 1) Is TA useful as a biologically-based flame retardant epoxy resin when it is surface functionalized with epoxy resin and then hardened with commercially available epoxy hardeners? 2) Is TA useful as a biologically-sourced phenolic epoxy hardening agent for DGEBA? and 3) Will chemical functionalization of TA with acetic anhydride result in a thermoset epoxy system which can compete with commercially available flame retardant additives? These questions, if answered successfully, could result in the adoption of TA industrially as an epoxy additive and potentially decrease environmental impact, reduce toxicity of components, and result in a more sustainable epoxy thermoset industry overall.

Additionally, this dissertation will identify the ongoing work in the lab in this space. This inclues the work in dispersing TA into the thinning agent methylethylketone (MEK) in an effort to increase the mechanical properties of a thinned epoxy thermoset will be discussed. Another chapter on the ongoing work of dispering metal-TA complexes as anticorrosive waterborne epoxy pigments is included. This work, in tandem with the work above, shows the many uses of this molecule in epoxy thermosets and enhancing their innate properties with the goal of decreasing the environmental and health impacts of the epoxy industry.

1.4 References

1. Kuruppalil, Z. In *Green Plastics: An Emerging Alternative for Petroleum Based Plastics?*, IAJC-ASEE International Conference, Hartford, Connecticut, Hartford, Connecticut, 2011.

2. Kuruppalil, Z. In *Plastics packaging: the challenge of going green*, The First International Conference on Green and Sustainable Technology, University of North Carolina A&T, University of North Carolina A&T, 2011.

3. Mwanza, B. M.; Mbohwa, C., Drivers to sustainable plastic solid waste recycling: a review. *Procedia Manufacturing* **2017,** *8,* 649-656.

4. Peng, L.; Deng, Y.; Yi, P.; Lai, X., Micro hot embossing of thermoplastic polymers: a review. *Journal of Micromechanics and Microengineering* **2014,** *24*, 1-23.

5. Chen, Z.; Yang, F.; Meguid, S., Multi-level modeling of woven glass/epoxy composite for multilayer printed circuit board applications. *International Journal of Solids and Structures* **2014,** *51* (21-22), 3679-3688.

6. Haugan, E.; Per Dalsjo, P., Characterization of the material properties of two FR4 printed circuit board laminates. FFI Rapport, 2014.

7. Composite Adhesives Market by Resin (Epoxy, Polyurethane), Component (One-Component, Two-Component), Application (Automotive & Transportation, Marine, Aerospace, Wind Energy), and Region - Global Forecast to 2022. (accessed October 4).

8. Wang, H.-h.; Zhou, X.-r.; Liu, Q.; Chen, G.-Q., Biosynthesis of polyhydroxyalkanoate homopolymers by Pseudomonas putida. *Applied Microbiology and Biotechnology* **2011,** *89* (5), 1497-1507.

9. Liu, Q.; Luo, G.; Zhou, X. R.; Chen, G.-Q., Biosynthesis of poly(3-hydroxydecanoate) and 3-hydroxydodecanoate dominating polyhydroxyalkanoates by β-oxidation pathway inhibited Pseudomonas putida. *Metabolic Engineering* **2011,** *13* (1), 11-17.

10. Chen, G.-q., A microbial polyhydroxyalkanoates (PHA) based bio- and materials industry. *Chemical Society Reviews* **2009,** *38* (8), 2434-2446.

11. Chen, G.-q.; Wang, Y., Medical applications of biopolyesters polyhydroxyalkanoates. *Chinese Journal of Polymer Science* **2013,** *31* (5), 719-736.

12. Guo-Qiang, C.; Patel, M. K., Plastics derived from biological sources: present and future: a technical and environmental review.(Report). *Chemical Reviews* **2012,** *112* (4), 2082-2099.

13. Chen, G.-Q., *Plastics from Bacteria Natural Functions and Applications*. Berlin, Heidelberg : Springer Berlin Heidelberg: 2010.

14. Burk, M., Sustainable production of industrial chemicals from sugar. *International Sugar Journal* **2010,** *112*, 30-35.

15. Minh, D. P.; Besson, M.; Pinel, C.; Fuertes, P.; Petitjean, C., Aqueous-Phase Hydrogenation of Biomass-Based Succinic Acid to 1,4-Butanediol Over Supported Bimetallic Catalysts.(Report). *Topics in Catalysis* **2010,** *53* (15 18), 1270.

16. Yuan, G. Z.; Tian, J.; Xu, L.; Tang, P.; B, C. D.; W, X. G., Fermentative production of PDO from glycerol by Aspergillus. *Food Ferment Ind* **2006,** *32* (1), 49-52.

17. Huang, Y.; Li, H.; Huang, X.; Yu, Y., Advances of Bio-ethylene. *Chinese Journal of Bioprocess Engineering* **2008,** *6*, 1-6.

18. Tsao, U.; Zasloff, H. B. Production of ethylene from ethanol. 1979.

19. Shota, A.; Taizo, H.; James, C. L., Non-fermentative pathways for synthesis of branched-chain higher alcohols as biofuels. *Nature* **2008,** *451* (7174), 86.

20. Luo, X.; Tang, D.; Li, M., Quantum investigation on the mechanism of isomerization of 1-butylene catalyzed by Rh-complex. *Journal of Molecular Structure: THEOCHEM* **2005,** *731* (1), 139-147.

21. Li, X.; Guan, J.; Zheng, A.; Zhou, D.; Han, X.; Zhang, W.; Bao, X., DFT studies on the reaction mechanism of cross-metathesis of ethylene and 2-butylene to propylene over heterogeneous Mo/HBeta catalyst. *Journal of Molecular Catalysis. A, Chemical* **2010,** *330* (1), 99-106.

22. Shen, L.; Patel, M. K., Life Cycle Assessment of man-made cellulose fibres. **2010**.

23. Ryan, C., Biobutanol potential for bio-based monomers and polymers. In *Emerging Trends in Single and Multi-Use Plastic Packaging*, Atlanta, GA, 2010.

24. Nasiri, M.; Reineke, T. M., Sustainable glucose-based block copolymers exhibit elastomeric and adhesive behavior. *Polym. Chem.* **2016,** *7* (33), 5233-5240.

25. Drumright, R. E.; Gruber, P. R.; Henton, D. E., Polylactic Acid Technology. *Advanced Materials* **2000,** *12* (23), 1841-1846.

26. Wanamaker, C. L.; Leary, L. E.; Lynd, N. A.; Hillmyer, M. A.; Tolman, W. B., Renewable-resource thermoplastic elastomers based on polylactide and polymenthide. *Biomacromolecules* **2007,** *8* (11), 3634.

27. Hillmyer, M. A.; Tolman, W. B., Aliphatic polyester block polymers: renewable, degradable, and sustainable. *Accounts of chemical research* **2014,** *47* (8), 2390.

28. Ding, K.; John, A.; Shin, J.; Lee, Y.; Quinn, T.; Tolman, W. B.; Hillmyer, M. A., High-Performance Pressure-Sensitive Adhesives from Renewable Triblock Copolymers. *Biomacromolecules* **2015,** *16* (8), 2537.

29. Lee, S.; Yuk, J. S.; Park, H.; Kim, Y.-W.; Shin, J., Multiblock Thermoplastic Elastomers Derived from Biodiesel, Poly(propylene glycol), and l -Lactide. *ACS Sustainable Chemistry & Engineering* **2017,** *5* (9), 8148-8160.

30. Xu, X.; Lin, J.; Cen, P., Advances in the Research and Development of Acrylic Acid Production from Biomass 1 1 Supported by the Special Funds for Major State Basic Research Program of China (973 Program, No.2004CCA05500). *Chinese Journal of Chemical Engineering* **2006,** *14* (4), 419-427.

31. Nexant, From Diapers to Paints - Is Bio-Acrylic Acid on the Way? *Prospectus* **2013**.

32. Voelker, F.; Figge, R.; Soucaille, P. Use of sucrose as substrate for fermentive production of 1,2-propanediol. EP2346999B1, 2013.

33. Cameron, D. C.; Altaras, N. E.; Hoffman, M. L.; Shaw, A. J., Metabolic Engineering of Propanediol Pathways. *Biotechnology Progress* **1998,** *14* (1), 116-125.

34. Altaras, N. E.; Cameron, D. C., Enhanced Production of (R)-1,2-Propanediol by Metabolically Engineered Escherichia coli. *Biotechnology Progress* **2000,** *16* (6), 940-946.

35. Fischer, R. H.; Pinkos, R.; Stein, F. Method for producing 1,6-hexanediol and 6-hydroxycaproic acid or their esters. 2002.

36. Theodore, H.; Tatum, H. W. Process for producing hexamethylenediamine from 1-6-hexanediol. 1966.

37. Teruyuki, N.; Wada, M.; Mizuta, H. Preparation process of aliphatic isocyanate. 1992.

38. Papa, A. J.; Kaiser, S. W. Preparation of isophorone and misityl oxide from acetone. 1985.

39. Pascault, J.-P.; Williams, R. J. J., Concepts about Epoxy Polymers, in Epoxy Polymers: New Materials and Innnovations. Wiley-VCH Verlag GmbH & Co.: 2010.

40. Li, Y.; Xiao, F.; Moon, K.; Wong, C., Novel curing agent for lead-free electronics: Amino acid. *Journal of Polymer Science Part a-Polymer Chemistry* **2006,** *44* (2), 1020-1027.

41. Pascault, J.-P.; Williams, R. J. J., Chap 1. General Concepts about Epoxy Polymers in Epoxy Polymers. *Epoxy Polymers: New Materials and Innovation* **2010**, 4.

42. Hsiao, K.; Alms, J.; Advani, S., Use of epoxy/multiwalled carbon nanotubes as adhesives to join graphite fibre reinforced polymer composites. *Nanotechnology* **2003,** *14* (7), 791-793.

43. Chortis, D. I., Structural Analysis of Composite Wind Turbine Blades. **2013,** *1*, 1--8.

44. Alapati, S.; Thomas, M., Influence of nano-fillers on electrical treeing in epoxy insulation. *Iet Science Measurement & Technology* **2012,** *6* (1), 21-28.

45. Epoxy coating market analysis by product by application and segment forecasts to 2024. (accessed September 25).

46. Epoxy Resin Market Projected To Reach $14.26 Billion By 2024. (accessed October 4).

47. Ehrler, S., The compatibility of epoxy-based printed circuit boards with lead free assembly. *Circuit World* **2005,** *31* (4), 3-13.

48. Masterbond EP62-1 Product Information.

49. Masterbond UV25 Product Information.

50. Baroncini, E.; Yadav, S.; Palmese, G.; Stanzione, J., Recent advances in bio-based epoxy resins and bio-based epoxy curing agents. *Journal of Applied Polymer Science* **2016,** *133* (45).

51. Takacs, E.; Vlachopoulos, J., Biobased, Biodegradable Polymers for Biomedical Applications: Properties and Process ability. *Plastics Engineering* **2008,** *64* (9), 28-33.

52. Shabestari, M. E.; Kalali, E. N.; González, V. J.; Wang, D.-Y.; Fernández-Blázquez, J. P.; Baselga, J.; Martin, O., Effect of nitrogen and oxygen doped carbon nanotubes on flammability of epoxy nanocomposites. *Carbon* **2017,** *121* (C), 193-200.

53. Zhou, Y.; Feng, J.; Peng, H.; Qu, H.; Hao, J., Catalytic pyrolysis and flame retardancy of epoxy resins with solid acid boron phosphate. *Polymer Degradation and Stability* **2014,** *110*, 395-404.

54. Inoue, K.; Sakamoto, T.; Min, J.; Todoroki, K.; Toyo'oka, T., Determination of dicyandiamide in infant formula by stable isotope dilution hydrophilic interaction liquid chromatography with tandem mass spectrometry. *Food Chemistry* **2014,** *156*, 390-393.

55. Smith, I.; Schallenberg, M., Occurrence of the agricultural nitrification inhibitor, dicyandiamide, in surface waters and its effects on nitrogen dynamics in an experimental aquatic system. *Agriculture Ecosystems & Environment* **2013,** *164*, 23-31.

56. S, O.; T, S.; N, S.; H, O.; H, N.; M, O.; M, M.; E, N., Subacute toxicity of an amine-curing agent for epoxy resin. *Sangyo Igaku* **1984,** *26* (3), 197-204.

57. Bastian, P., Occupational hepatitis caused by methylenedianiline. *Medical Journal of Australia* **1984,** *141* (8), 533-535.

58. Fishback, T.; McMillinl, C.; Farona, M., A new, non-toxic, curing agent for synthetic polyolefins. *Biomedical Materials Engineering* **1992,** *2* (2), 83-87.

59. Park, S.-J.; Jin, F.-L.; Lee, J.-R., Thermal and mechanical properties of tetrafunctional epoxy resin toughened with epoxidized soybean oil. *Materials Science & Engineering A* **2004,** *374* (1-2), 109-114.

60. Zhu, J.; Chandrashekhara, K.; Flanigan, V.; Kapila, S., Curing and mechanical characterization of a soy-based epoxy resin system. *Journal of Applied Polymer Science* **2004,** *91* (6), 3513-3518.

61. Hong, J.; Radojčić, D.; Ionescu, M.; Petrović, Z. S.; Eastwood, E., Advanced materials from corn: Isosorbide-based epoxy resins. *Polymer Chemistry* **2014,** *5* (18), 5360-5368.

62. Cho, J. K.; Lee, J.-S.; Jeong, J.; Kim, B.; Kim, B.; Kim, S.; Shin, S.; Kim, H.-J.; Lee, S.-H., Synthesis of carbohydrate biomass-based furanic compounds bearing epoxide end group(s) and evaluation of their feasibility as adhesives. *Journal of Adhesion Science and Technology* **2013,** *27* (18-19), 2127-2138.

63. Nouailhas, H.; Aouf, C.; Le Guernevé, C.; Caillol, S.; Boutevin, B.; Fulcrand-Hoh, H. H., Synthesis and Properties of Biobased Epoxy Resins. Part 1. Glycidylation of Flavonoids by Epichlorohydrin. *Journal of polymer science: Part A, General papers* **2011,** *49* (10), 2261-2270.

64. Mathew, V. S.; George, S. C.; Parameswaranpillai, J.; Thomas, S., Epoxidized natural rubber/epoxy blends: Phase morphology and thermomechanical properties. *Journal of Applied Polymer Science* **2014,** *131* (4), n/a-n/a.

65. Ferdosian, F.; Yuan, Z.; Anderson, M.; Xu, C. C., Chemically modified lignin through epoxidation and its thermal properties. *J-FOR* **2012,** *2* (4), 11-15.

66. Liu, X. Q.; Huang, W.; Jiang, Y. H.; Zhu, J.; Zhang, C. Z., Preparation of a bio-based epoxy with comparable properties to those of petroleum-based counterparts. *eXPRESS Polymer Letters* **2012,** *6* (4), 293-298.

67. Xiaosu, Y.; Konstantinos, T., Special Issue "ECO-COMPASS: Ecological and Multifunctional Composites for Application in Aircraft Interior and Secondary Structures". *Aerospace* **2019,** *6* (2), 17.

68. Stemmelen, M.; Lapinte, V.; Habas, J.; Robin, J., Plant oil-based epoxy resins from fatty diamines and epoxidized vegetable oil. *European Polymer Journal* **2015,** *68*, 536-545.

69. Jaillet, F.; Darroman, E.; Ratsimihety, A.; Auvergne, R.; Boutevin, B.; Caillol, S., New biobased epoxy materials from cardanol. *European Journal of Lipid Science and Technology* **2014,** *116* (1), 63-73.

70. Hu, F., Preparation and Characterization of Fully Furan-Based Renewable Thermosetting Epoxy-Amine Systems. **2015**, 1441--1446.

71. Fache, M.; Monteremal, C.; Boutevin, B.; Caillol, S., Amine hardeners and epoxy cross-linker from aromatic renewable resources. *European Polymer Journal* **2015,** *73*, 344-362.

72. Takahashi, T., Biocomposites Composed of Epoxidized Soybean Oil Cured with Terpene-Based Acid Anhydride and Cellulose Fibers. **2008**.

73. Metkar, P.; Scialdone, M.; Moloy, K., Lysinol: a renewably resourced alternative to petrochemical polyamines and aminoalcohols. *Green Chemistry* **2014,** *16* (10), 4575-4586.

74. Motahari, A., On the Thermal Degradation of a Novel Epoxy- Based Nanocomposite Cured With Tryptophan as an Environment-Friendly Curing Agent On the Thermal Degradation of a Novel Epoxy- Based Nanocomposite Cured With Tryptophan as an Environment-Friendly Curing Agent. **2015,** *2348* (June 2017).

75. Ma, S.; Webster, D., Naturally Occurring Acids as Cross-Linkers To Yield VOC-Free, High-Performance, Fully Bio-Based, Degradable Thermosets. *Macromolecules* **2015,** *48* (19), 7127-7137.

76. Jaillet, F.; Desroches, M.; Auvergne, R.; Boutevin, B.; Caillol, S., New biobased carboxylic acid hardeners for epoxy resins. *European Journal of Lipid Science and Technology* **2013,** *115* (6), 698-708.

77. Okuda, T.; Ito, H., Tannins of Constant Structure in Medicinal and Food Plants-Hydrolyzable Tannins and Polyphenols Related to Tannins. *Molecules* **2011,** *16* (3), 2191-2217.

78. Doat, J., Tannins in tropical woods. [Samples of Mangroves (Rhizophora spp.) and certain Eucalyptus]. *Tannins in tropical woods. [Samples of Mangroves (Rhizophora spp.) and certain Eucalyptus]* **1978,** (no), 37-54.

79. Clifford, M. N., Diet-Derived Phenols in Plasma and Tissues and their Implications for Health. *Planta Medica* **2004,** *70* (12), 1103-1114.

80. McRae, J.; Kennedy, J., Wine and Grape Tannin Interactions with Salivary Proteins and Their Impact on Astringency: A Review of Current Research. *Molecules* **2011,** *16* (3), 2348-2364.

81. Puupponen-Pimiä, R.; Nohynek, L.; Hartmann-Schmidlin, S.; Kähkönen, M.; Heinonen, M.; Määttä-Riihinen, K.; Oksman-Caldentey, K. M., Berry phenolics selectively inhibit the growth of intestinal pathogens. *Journal of Applied Microbiology* **2005,** *98* (4), 991-1000.

82. Olajire, A. A., The brewing industry and environmental challenges. *Journal of Cleaner Production* **2012**.

83. Roberts, M., Edwin Haslam. Plant Polyphenols—Vegetable Tannins Revisited Cambridge University Press, Cambridge, 1989. £37.50. *Phytotherapy Research* **1990,** *4* (4), ii-ii.

84. Hemingway, R. W.; Karchesy, J. J.; Branham, S. J., 1st North American Tannin Conference, Port Angeles, Wash. (USA), 1988. In *Chemistry and significance of condensed tannins*, Plenum Press: New York (USA), 1989.

85. Ciocan, D.; Ioan, B., PLANT PRODUCTS AS ANTIMICROBIAL AGENTS. *Analele Stiintifice ale Universitatii "Al. I. Cuza" Din Iasi. (Serie Noua). Sectiunea 2.a. Genetica si Biologie Moleculara* **2007,** *8* (1).

86. Wilson, W. C.; Macgregor, A. R.; Stewart, C. P., The clinical course and pathology of burns and scalds under modern methods of treatment. *British Journal of Surgery* **1938,** *25* (100), 826-865.

87. Wilson, H. L., Investigation into non-aqueous remedial conservation treatments for iron-tannate dyed organic materials. Carr, C.; Rigout, M., Eds. University of Manchester: 2013.

88. Phiwchai, I.; Yuensook, W.; Sawaengsiriphon, N.; Krungchanuchat, S.; Pilapong, C., Tannic acid (TA): A molecular tool for chelating and imaging labile iron. *European Journal of Pharmaceutical Sciences* **2018,** *114,* 64-73.

89. Gülçin, İ.; Huyut, Z.; Elmastaş, M.; Aboul-Enein, H. Y., Radical scavenging and antioxidant activity of tannic acid. *Arabian Journal of Chemistry* **2010,** *3* (1), 43-53.

90. Xia, Z.; Singh, A.; Kiratitanavit, W.; Mosurkal, R.; Kumar, J.; Nagarajan, R., Unraveling the mechanism of thermal and thermo-oxidative degradation of tannic acid. *Thermochimica Acta* **2015,** *605,* 77--85.

91. Xia, Z.; Kiratitanavit, W.; Facendola, P.; Thota, S.; Yu, S.; Kumar, J.; Mosurkal, R.; Nagarajan, R., Fire resistant polyphenols based on chemical modification of bio-derived tannic acid. *Polymer Degradation and Stability* **2018,** *153,* 227-243.

92. Grigsby, W. J.; Kadla, J. F., Evaluating Poly(lactic acid) Fiber Reinforcement with Modified Tannins. *Macromolecular Materials and Engineering* **2014,** *299* (3), 368-378.

93. Korey, M.; Mendis, G. P.; Youngblood, J. P.; Howarter, J. A., Tannic acid: A sustainable crosslinking agent for high glass transition epoxy materials. *Journal of Polymer Science Part A: Polymer Chemistry* **2018,** *56* (13), 1468-1480.

94. Qi, M.; Xu, Y.-J.; Rao, W.-H.; Luo, X.; Chen, L.; Wang, Y.-Z., Epoxidized soybean oil cured with tannic acid for fully bio-based epoxy resin. *RSC Adv.* **2018,** *8* (47), 26948-26958.

95. Karaseva, V.; Bergeret, A.; Lacoste, C.; Fulcrand, H.; Ferry, L., New biosourced flame retardant agents based on gallic and ellagic acids for epoxy resins. *Molecules* **2019,** *24* (23).

96. Kim, Y. O.; Cho, J.; Yeo, H.; Lee, B. W.; Moon, B. J.; Ha, Y. M.; Jo, Y. R.; Jung, Y. C., Flame Retardant Epoxy Derived from Tannic Acid as Biobased Hardener. *ACS Sustainable Chemistry and Engineering* **2019,** *7* (4), 3858-3865.

97. Shibata, M.; Teramoto, N.; Makino, K., Preparation and Properties of Biocomposites Composed of Epoxidized Soybean Oil, Tannic Acid, and Microfibrillated Cellulose. *Journal of Applied Polymer Science* **2011,** *120* (1), 273-278.

98. Fei, X.; Zhao, F.; Wei, W.; Luo, J.; Chen, M.; Liu, X., Tannic Acid as a Bio-Based Modifier of Epoxy/Anhydride Thermosets. *Polymers* **2016,** *8* (9).

2. TANNIC ACID BASED PRE-POLYMER SYSTEMS FOR ENHANCED INTUMESCENCE IN EPOXY THERMOSETS

This chapter is based upon work that is currently under review for *Green Materials* (2020) special edition on flame retardants in polymers. This chapter is also based off of work that was previously published in the conference proceedings for REWAS, TMS 2019. This chapter is reproduced with permission.

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For the work showed in this chapter I wrote all of the text apart from Section 2.3, and performed all of the tests except for FTIR analysis, and mechanical testing. These sections are based off of work performed by Bill Webb and Chuck Loney, who were undergraduate and guest researchers who collaborated with me on this work.

2.1 Abstract

Tannic acid (TA) is a bio-based high molecular weight organic (HMWO), aromatic molecule. Although biologically sourced, TA is a pollutant in industrial wastewater streams, and there is desire to find applications in which to downcycle this molecule after extraction from these streams. Many flame retardants (FR) used in epoxy thermosets are synthesized from petroleum-based monomers leading to significant environmental impacts at the industrial scale. Various bio-based modifiers have been developed to improve the FR of the epoxy resin; however, increasing FR of the system without tradeoffs with other properties, especially mechanical properties and glass transition temperatures, has proven challenging. In this work, TA is reacted with epoxy resin and thereby incorporated into the thermoset. The molecular behavior of the system was found to change based on TA loading level, with very low concentrations causing the molecule to be surface functionalized while at higher concentrations the molecule was crosslinked into a pre-thermoset network. After additional hardening using a commercial hardening agent, the material was further characterized for its crosslink density, thermal stability, mechanical and thermomechanical properties, and FR ability. In this work, because the molecule was surface-functionalized or pre-

reacted, TA was found to work well as an intumescent agent but did not reduce the heat release rate of the fire. The results of this study suggest that the external (hydrophilic surface-phenol groups) and internal (d-glucose and attached phenyl groups) structural regions of the TA molecule impact the FR ability of the molecule in epoxy separately. Maintaining the structural integrity of both regions is critical to the synergistic FR behavior of the molecule.

2.2 Introduction

After the initiation of a fire, it is estimated that in a modern home the individual has 3 minutes to evacuate, an amount of time which has significantly decreased since the mid-20th Century.[1, 2] The reduction in fire escape times is largely due to the change in household materials from more natural, plant-based wood and fibers to more flammable materials such as plastics and synthetic fibers and foams that are used currently in many consumer, domestic products.[3] There are two main types of plastics in use in the modern home: 1) thermoplastics, such as nylon, polyethylene, and polystyrene which are used in many applications such as insulation, packaging, and casings, and 2) thermosets, such as polyurethane, polyurea, and epoxy which are used in many other applications including floor coatings, pipe linings, and electronics.[4-8] In 2015, the global demand for plastic exceeded 300 million tons, and this value is growing steadily at an average rate of 3.4%, with US plastics companies employing over 1 million workers and providing nearly $400 billion in annual shipments.[9, 10] The vast majority of plastics are synthesized from precursor chemicals which are industrially sourced from petroleum during the refining process.[11, 12] For this reason, it is unsurprising that these chemicals would cause concern with flammability in domestic applications and decrease the time to evacuate.

Although the adoption of flame retardants in industry has led to a significantly increased time to evacuate, there are significant concerns with the toxicity of these chemicals, especially at the end of the life of the material.[13, 14] Although it is expected that in most materials the resulting composite would be inert and benign, this is in fact not the case. Research shows that these FR additives, other additives, and un-reacted monomer or pre-cursor units in plastics leech out during the lifetime of the consumer product, and then after the product is put into the waste stream resulting in many of these compounds entering into the potable water supply.[15-17] This is particularly concerning as, in most plastics, FR additives are loaded between 2-60 wt% into the system, making them often a considerable amount of the weight of the polymer.[18, 19] More recent research has shown that bioaccumulation of FRs in humans can lead to delayed growth, thyroid alterations, ADHD, poor social complexity symptoms, and even cancer.[20] Furthermore, the health impacts of flame retardants are felt more strongly in less-wealthy regions of the world where individuals are found to have elevated concentrations of FRs in breast milk and water.[21] In response to this, researchers have developed synthetic, non-brominated, flame retardant alternative compounds, but these compounds still bioaccumulate, require similar loading levels if not higher than their counterpoints, and have high persistence and toxicity in the environment and human health.[14] Ongoing research shows that there is a significant need for non-toxic, non-synthetic alternative flame retardants to minimize toxicity at the end of life of products. For this, most researchers have turned to biologically-sourced compounds to minimize the effects to humans and the environment downstream when leeching inevitably occurs.

There is currently ongoing research on biologically based flame retardant additives in the literature, including molecules such as cellulose, deoxyribonucleic acid, lignins, starch, clay, condensed tannins and tannic acid (TA) but these compounds are often limited in application by solubility mis-matches between compounds and hydrophobic polymer systems.[22-28] There is currently a wealth of literature on biologically-based flame retardant alternatives for thermoplastic materials, but there are very few currently in use for thermoset materials, especially for epoxy. Epoxy is a thermoset material that is formed by the reaction of a diglycidylated compound, often the diglycidyl ether of bisphenol A (DGEBA), and a multi-functional hardening agent that can be aminated, sulfonated, acid-based, or even phenol based among other functionalities. Epoxy materials are used in a variety of domestic applications including electronics, floor coatings, and domestic potable water pipe linings.[8, 29, 30] The addition of epoxy into domestic applications is at least partially responsible for the decrease in domestic evacuation times described in literature, and the use of flame retardants in this material, especially in electronic circuit boards and domestic coatings, is a well known method to decrease its flammability.[13, 31, 32]

There is a need for researchers to develop methods to increase dispersibility of biologically-based flame retardant alternatives in epoxy without the need for chemical modification or solvent. However, there is very limited research in this topic for several bio-based chemicals above, especially TA. TA is a biologically-sourced antioxidant found in nuts, galls, seeds, and tree bark that is FDA approved to be consumed by humans and is generally regarded as safe (GRAS). TA has been explored as an additive in a variety of polymer matrices including poly(lactic acid), nylons, formaldehyde-based polymers, polyesters, and urethane foams.[33-41] It has previously been explored as a functional additive in epoxy, but not for its intumescent ability in this polymer which is mostly due to the significant compatibility mis-match between TA and epoxy.[32] Previous researchers have combated these compatibility limitations in many polymer systems by use of chemical modification, and were able to achieve high loading levels of TA up to 50% in many polymer systems.[35, 40-42] Previous work determined methods for dispersing high-concentrations of unmodified TA in epoxy while still maintaining good compatibility without the use of solvent or chemical modification. However, this work did not explore the flame retardancy of the molecule in epoxy, which is a potentially missed advantage of using TA as a hardening agent in epoxy.

The purpose of this work is to determine the chemical interactions at low loading levels of TA in DGEBA with the hope of developing an ideal pre-thermoset resin of reacted TA and DGEBA without producing a polymer that is too viscous to be further hardened, as is the case with epoxy samples containing TA at 9 %wt or higher. Further, to meet the knowledge gap in the scientific literature, the flame retardancy of the resulting thermoset was studied. The resulting pre-polymer resin shows promise for use in this application and will hopefully reduce the impact of the flame-retardant intumescent additives on human health and the environment.

2.3 Methods

2.3.1 Materials

TA was purchased from Sigma Aldrich (St. Louis, MO, USA). EPON 825 (DGEBA) resin was purchased from Hexion, Inc. (Louisville, KY, USA). Mold Max 60 silicone precursor and initiator (parts A and B) were purchased from Smooth-On, Inc. (Macungie, PA, USA) GP2074 novolac resin was purchased from Georgia Pacific (Atlanta, GA, USA). 20mL borosilicate scintillation vials were purchased from Thermo Fisher Scientific (Waltham, MA, USA). Poly(tetrafluoroethylene) magnetic stir bars were purchased from Carolina Biological Supply Company (Burlington, NC, USA).

2.3.2 Composite Positive Mold Preparation for Plaques and Bars

A 3D design of a composite block was created using Fusion 360 to make the necessary silicone molds. A ramp on the side of each mold was included that serves as a starting point when taking silicone out of the mold to prevent ripping the silicone. About ½ inch of space on each side of each positive mold was created, and about ¼ inch on top of the mold was designed to create the bottom for the silicone mold to be generated later. A CAM process in Fusion 360 used to machine all the corners on the composite using a sheet router. An orbital sander was used to sand down the top surface of each plaque or bar using 220 grit sandpaper. This allowed silicone to separate from the composite positive mold more easily, and the epoxy to separate more easily from the silicone negative mold later. The mold was sprayed with air to remove any unwanted composite dust.

2.3.3 Silicone Mold Preparation

750g of Mold Max-60 Part A (Smooth-On Silicone Rubber Compound) was poured into a large beaker and the mass was measured and recorded. The amount of Mold Max Part B (Smooth-On Silicone Rubber Compound) to combine with Part A (100A/3B ratio by mass) was calculated and poured into the beaker then mixed thoroughly until the mixture was a homogeneous red color. The composite positive molds for each batch of epoxy were prepared by spraying with mold release (Stoner E206 Silicone Mold Release), then the Mold Max-60 mixture was poured into the that mold until it was filled to the top edges. The silicone mold was allowed to cure for at least 12 hours at room temperature on a flat surface.

2.3.4 TA-DGEBA Heating

About 150g of DGEBA resin (Hexion Epon 825 Resin) was poured into a clean and dry beaker, and the mass was measured and recorded. The corresponding mass of TA to mix into the resin based on the desired percentages (0.1, 0.32, 1, 3.2, 5, 6, 7, and 8%) was calculated and added to the resin in a Nalgene container. The Nalgene container was sealed and placed in the FlackTek SpeedMixer using the 400 max-100 holder for a 10 minute mixing cycle (3min at 1600rpm, 30s at 0rpm, 3min at 1600rpm, 30s at 0rpm, 3min at 1600rpm). The mixture was then poured into a 250mL beaker with a magnetic stir bar and placed in a hot oil bath at 105°C for 3 hours with constant stirring. Samples with higher weight percentages than 8wt% TA were not studied in this procedure as during this heating step, samples became too viscous to mix, which is consistent with previous literature. After 3 hours, the mixture was removed from the hot oil bath and allowed to cool for approximately 20 minutes. Once cool, TA-DGEBA resin mixture was poured into an aluminum foil container and heated in the oven at 150°C for 4 hours. After heating, the mixture was allowed to cool to room temperature and stored for future epoxy creation.

2.3.5 Epoxy Sample Preparation

The silicone negative molds for each batch of epoxy were prepared by spraying with mold release (Stoner E-206 Silicone Mold Release), heating for five minutes at 80°C then spraying again. The desired TA-DGEBA epoxy resin was prepared for hardening with GP2074 by measuring out approximately 54g into a Nalgene container and the mass was recorded precisely. The GP2074 resin was ground up using a mortar and pestle prior to mixing. The Nalgene container was sealed and placed in the FlackTek SpeedMixer without any milling media using the 400 max-100 holder for the same 10 minute mixing cycle as the TA-DGEBA resin synthesis described above. The mixture was then poured into a 250mL beaker with a stir bar and heated in an oil bath at 65°C for 13 minutes plus 1 extra minute for every percent of TA in solution with the stir bar spinning continuously. Every 2 or 3 minutes the mixture was monitored, and the stirring speed was increased as the viscosity of mixture decreased. After removing the beaker from the oil bath, the mixture was poured into the silicone molds using a clean spatula. Next, the epoxies were placed in the oven for a 12-hour curing program: warm for 1 hour from 80°C to 140°C, hold at 140°C for 3 hours, warm to 160°C over the course of 1 hour, hold at 160°C for 2 hours, cool to room temperature over the course of 5 hours (Figure 3).

2.3.6 Epoxy Sample Characterization

Optical Microscopy was performed using a Zeiss optical microscope (Zeiss, Thornwood, NY, USA). Samples prepared for DMA were analyzed under the microscope to ensure uniform thickness between samples. Image analysis was done using ImageJ (National Institute of Health, Bethesda, MD, USA).

Ultraviolet-visible (UV/Vis) spectroscopy was performed using a Lambda 950 UV-VIS-NIR spectrophotometer (PerkinElmer, Waltham, MA, USA). Three samples at each concentration were prepared in acrylic cuvettes. All absorbance values were normalized to an empty cuvette. Transmission was measured for all wavelengths between 200-800 nm to measure the full visible light spectrum. Transmission curves were analyzed using OriginPro 2019 (OriginLab, Northampton, MA, USA). A UV-flashlight was also used to help characterize samples. An Optimax 365 UV-LED flashlight (Spectroline, Westbury, NY, USA) was pointed at the samples. The photo was taken using a PowerShot A70 Camera (Canon, Woodridge, IL).

Thermogravimetric analysis (TGA) was performed with a Q50 thermogravimetric analyzer (TA Instruments, Newcastle, DE, USA). Samples were prepared for TGA analysis by shaving off 15±2.3 mg of sample from epoxy products. Experiments were performed in nitrogen with a 60 mL/min flow rate using a 20 °C/min heating rate from 30 °C to 900 °C. Three epoxy samples were run at each concentration and results were averaged. T_d was determined by finding the peak of the mass loss rate curve using Universal Analysis (TA Instruments, Newcastle, DE, USA) and averaging the temperature values at this point. Remaining char values were calculated by measuring the weight fraction of the sample using Universal Analysis (TA Instruments, Newcastle, DE, USA) at the completion of the TGA test (800 °C) and then averaging the weight fraction values at this point.

Differential Scanning Calorimetry (DSC) was performed on liquid pre-polymer samples using a Q2000 Differential Scanning Calorimeter (TA Instruments, Newcastle, DE, USA). Samples of 12±1.2 mg were loaded into aluminum pans and run using a heat/cool/heat cycle from –75 °C to 200°C with a heating and cooling rate of 25 °C/min. Three samples were run at each concentration and the mean glass transition value of the curve was calculated as the midpoint of the incline/decline observed on thermograms and averaged for each concentration using Universal Analysis (TA Instruments, Newcastle, DE, USA).

Dynamic Mechanical Analysis (DMA) was performed on all samples using Q800 Dynamic Mechanical Analyzer (TA Instruments, Newcastle, DE, USA). Samples were prepared of dimensions 5.5 cm x 1.2 cm x 0.35 cm by pouring prepared solutions into silicone molds and then cured. Samples were polished to remove remaining silicone from their surfaces. A dual cantilever mechanical test was performed at a frequency of 1 Hz and displacement of 0.15 µm. Temperature was held constant at 30 °C and the storage modulus was measured for 20 minutes. Three samples were run at each TA concentration and were averaged. E' values were calculated by averaging the datapoints for all samples of the same wt%. TA using Universal Analysis (TA Instruments, Newcastle, DE, USA).

Fourier transform infrared (FTIR) spectroscopy was performed using a PerkinElmer Spectrum 100 FTIR Spectrometer (PerkinElmer, Seer Green, Beaconsfield, UK) outfitted using a zinc selenide (ZnSe) crystal. Samples were scanned from 650 cm$_{-1}$ to 4000 cm$_{-1}$ in transmissive mode. EPON 825 was heated at 400 °C for 1 hour in nitrogen atmosphere. A control EPON 825 sample at room temperature was isolated as well. TA/DGEBA composite samples were prepared by isolating shavings from the epoxy bars described previously. Samples were scanned 4 times and normalized to the phenyl peak at 1605 cm$_{-1}$ using Spectra (PerkinElmer, Seer Green, Beaconsfield, UK). Absorbance values were calculated using Spectra (PerkinElmer, Seer Green, Beaconsfield, UK) and were averaged between samples.

Mechanical testing was performed using a compression fixture on a Mechanical testing frame (MTS Instruments, Eden Prairie, MN, USA). Cylindrical samples were prepared with dimensions of 24.2 ± 1.3 mm X 30.1 ± 4.8 mm being diameter and height respectively. 5 samples were run at each concentration and they were loaded to break, which was determined by observable cracking and fracture on the surface of the part. Toughness values were obtained by integrating the stress/strain curves using OriginPro 2017 (OriginLab Inc., Northampton, MA, USA).

Statistical analysis was performed using JMP (SAS Institute, Cary, NC, USA). A student's t-test was run to compare samples. A p-value <0.05 was used to indicate statistically significant differences between samples. Regression analysis was performed using OriginPro 2017 (OriginLab Inc., Northampton, MA, USA). Results were fit to an exponential decay and linear models, and the reported equations and standard error (S_e) values were output by the software after regression analysis. S_e values <0.05 were determined as appropriate fits for the regression.

Mass loss calorimetry (MLC) was performed using an MLC 2004 mass loss calorimeter (Fire Testing Technologies, East Grinstead, UK) which was modified with a chimney and additional thermopiles. The procedure determined by Mendis et. al was performed.[31] Poly(methyl methacrylate), polystyrene, and ethylene glycol standards were used to calibrate the instrument. The heat source was set at 35 kW/m^2 and remained constant for the duration of the test. A spark igniter was used to ignite the samples. The test was concluded when the mass loss rate was less than 2.5 g/min. Five specimens were analysed for each composition and were prepared according to ASTM E 2102-15. Mass loss curves were analysed using OriginPro software.

2.4 Results and Discussion

2.4.1 Pre-polymer TA-DGEBA systems

TA has been found to react with epoxy groups as well as epoxy resin at elevated temperature. Verification of chemical modification through FTIR spectroscopy was performed (Figure 2.1 and Figure 2.2). The results from this study were consistent with previous literature indicating that TA did in fact react with the epoxy resin.

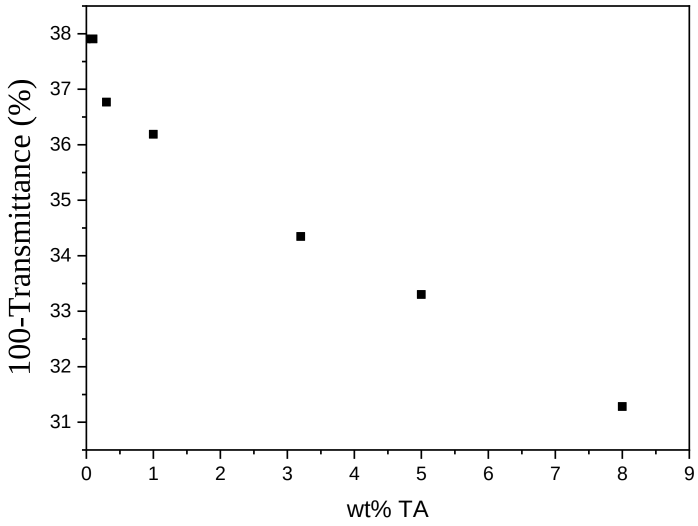

Figure 2.1: FTIR absorbance values after normalization to the C-H bond absorbance associated with the DGEBA molecule. Epon 825 was used as control sample, and the value of the epoxy ring at 915 cm-1 was utilized for this figure.

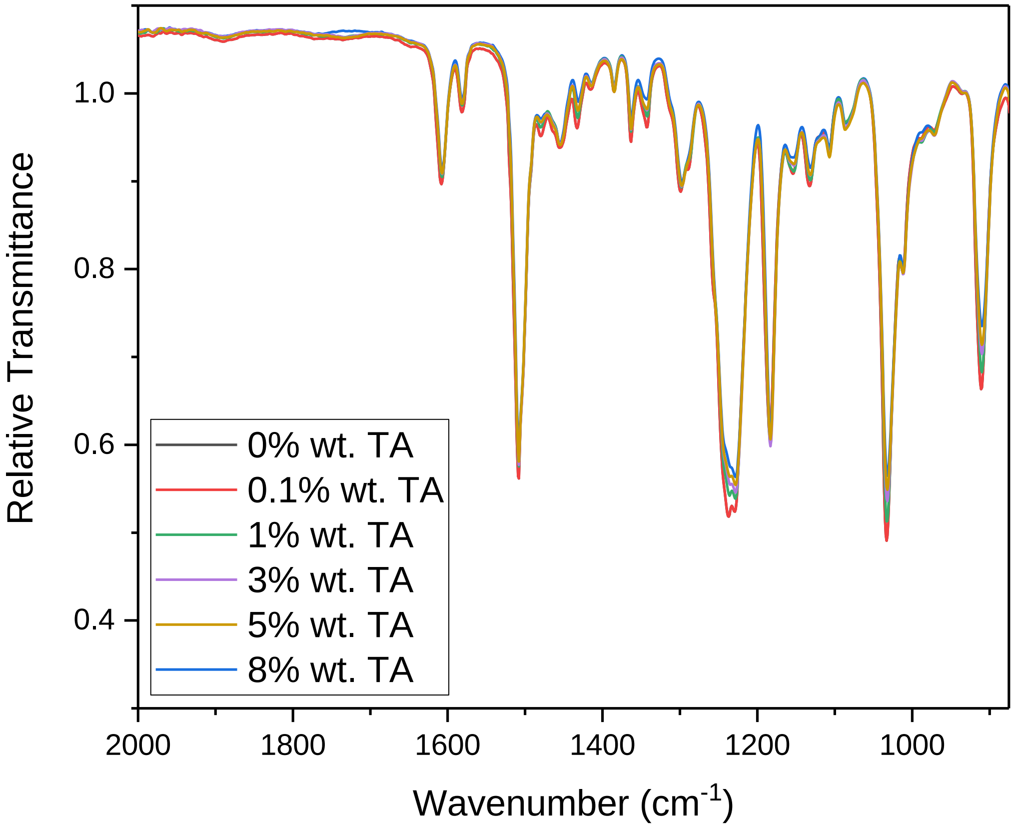

Figure 2.2: FTIR result of the fingerprint region of TA-DGEBA composites. After normalization to DGEBA resin, the epoxy ring peak is dependent upon TA-loading into the solution, indicating chemical reaction between TA and DGEBA at elevated temperature.

Samples were characterized using UV-vis to characterize their degree of "brown-ness" and to quantifiably measure the dispersion in the samples (Figure 2.3). This browning effect was expected and is the typical result of using tannins in polymer matrices.[32, 33, 36, 39, 41] Samples of 1 wt% TA or less were found to have transmittance values in the range of 80% or higher for all wavelengths in the visible light spectrum. However, at loading levels past 3 wt% TA, samples were found to have decreased transmittance at all wavelengths, and near 0% transmittance at all values below 410nm. On average, samples were found to have increased transmittance values at higher wavelengths associated with red, orange, and yellow light and absorb more light in the wavelengths associated with green, blue, violet light. This result is to be expected as samples appeared to "brown" with increased TA loading resulting in transmittance of colors which would produce brown. A UV-LED flashlight was shined on samples and showed that the change in transmittance was the result of agglomeration and not a change in absorbance (Figure 2.4)

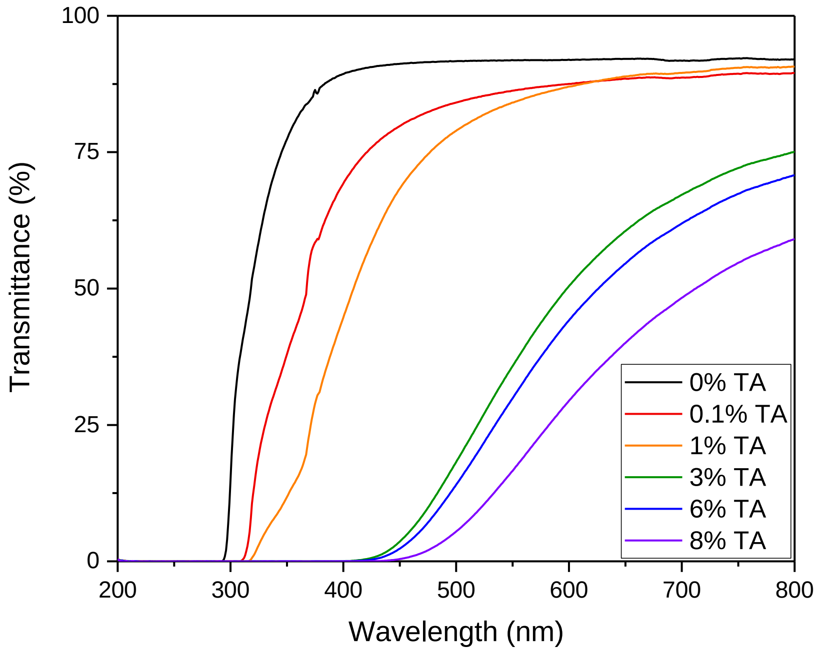

Figure 2.3 UV/Vis Absorbance curves for TA-loaded DGEBA pre-polymer resins.

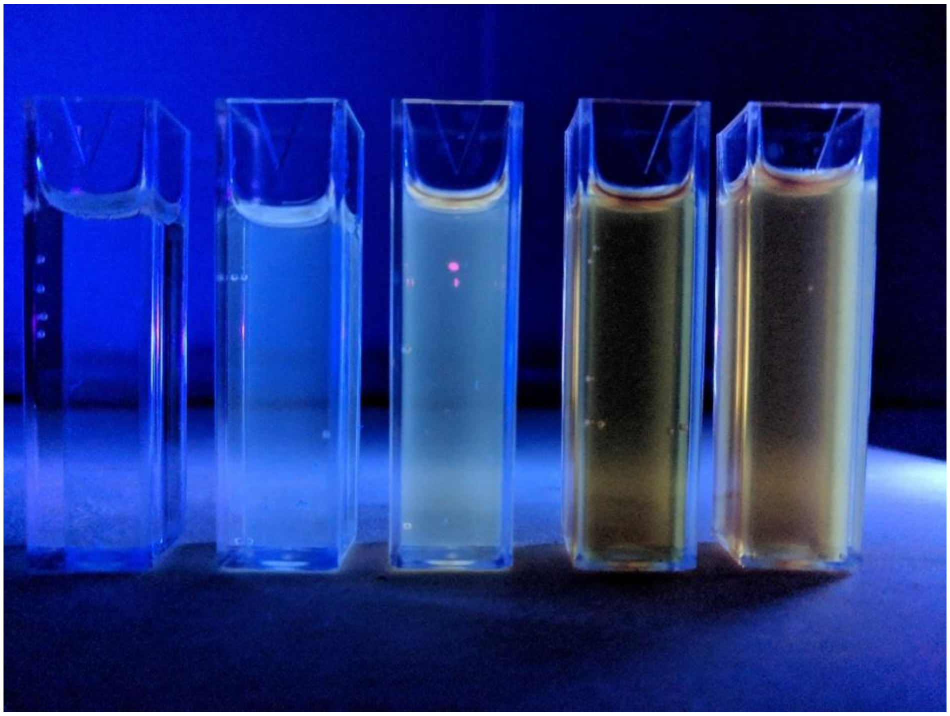

Figure 2.4: Samples observed at 365nm UV-light using a UV flashlight

To further understand the molecular interactions within the system, samples of the TA-DGEBA resin were analyzed using TGA (Figure 2.5). The results from TGA show that all samples containing TA and DGEBA have elevated temperatures of thermal degradation (T_d) as compared to either control. No significant differences were found between the temperature of degradation in any composite system, but the magnitude of the maximum value of the derivative weight curve decreased as the concentration of TA in the composite system increased. A second degradation was observed in all TADGEBA composites at 425°C and the magnitude of the maximum value of the derivative weight curve increased as the concentration of TA in the composite increased. This second peak did not correspond to TA, which indicates a more chemically stable complex of TA and DGEBA. The thermal degradation of the DGEBA control sample at 280°C has been found in literature to be associated with degradation of the epoxy rings within the molecule.[32] Similarly, the degradation of TA at 260°C has been found by previous research to be associated with the phenol groups on the molecule. No TA-DGEBA composite samples had thermal degradation peaks at either of these values and the peak temperatures of thermal degradation associated with these composites were significantly different from the controls, although the derivative weight curves were quite broad.

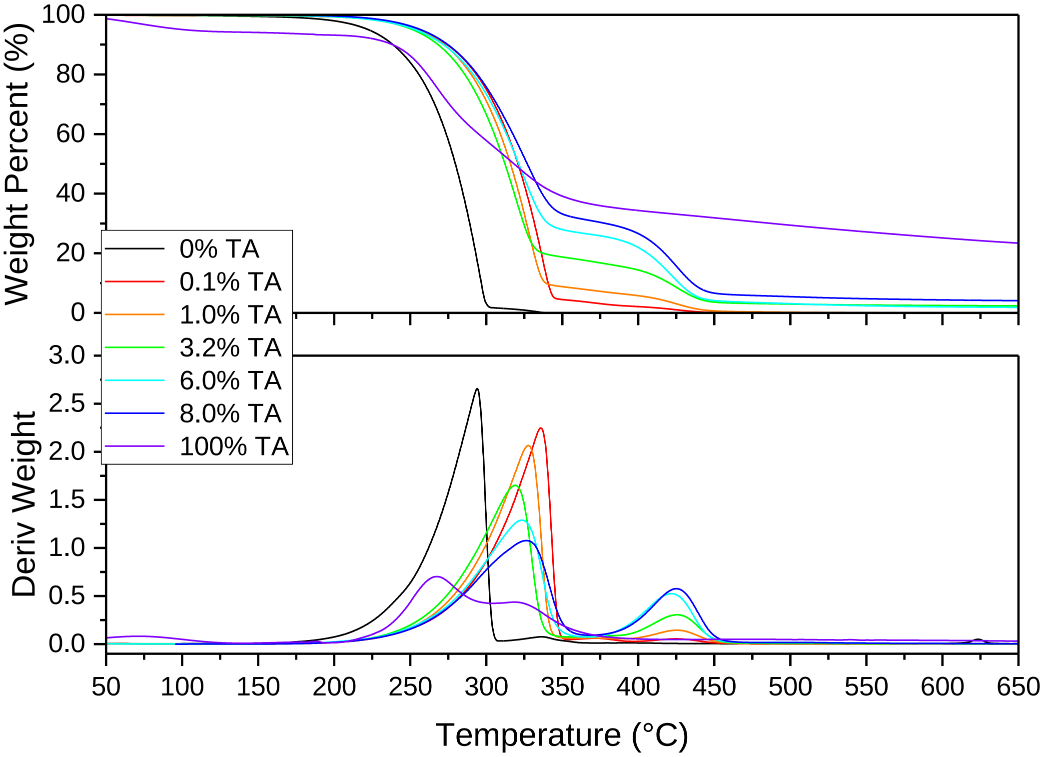

Figure 2.5: TGA thermograms of TA-DGEBA samples and controls

Samples were also analyzed using DSC (Figure 2.6). After crosslinking, all samples showed a glass transition temperature near -18°C regardless of TA-loading into solution, although the value was found to significantly increase in highly loaded TA samples (≥3 wt% TA)

(
Table 2.1). However, the control as well as samples containing ≤1 wt% TA were shown on the heat curve to have a melting temperature at 34°C, and no significant changes in melting temperature were observed from the control samples. However, the magnitude of the melting peak was increased in both the 0.1 and 1 wt% TA samples as compared to the control. Conversely, samples containing 3.2 wt% or more TA were found to have no melting peak during the heating cycle. There were no observed crystallization peaks on the cooling curve, although the glass transition was observed in all samples regardless of TA loading. For samples loaded at or below 1 wt% TA, there was no statistically significant increase in the T_g. However, for samples loaded at 3 wt% TA or higher, there was an observed significant increase in the T_g of samples as compared to the control.

Table 2.1: Preliminary characterization results of epoxy samples

% wt. TA	Glass Transition Temperature (°C)	Melting Temperature (°C)	Heat of Melting (J/g)	Thermal Decomposition Temperatures (°C)	Weight Fraction Surface Functionalized (ϕ_f)	Weight Fraction Crosslinked (ϕ_c)
0	-20.0 ± 1.5	42.4 ± 0.03	3.80 ± 0.8	293 ± 8.5 N/A	3.1 ± 0.23	--
0.1	-18.6 ± 1.6	42.5 ± 0.8	26.8 ± 3.5	331 ± 6.2* 425 ± 0.8	7.2 ± 0.24*	0.1 ± 0.02
1	-19.7 ± 0.5	40.1 ± 1.7	7.36 ± 1.8	324 ± 5.4* 426 ± 2.1	16.8 ± 0.88*	0.2 ± 0.01*
3	-16.3 ± 1.9*	--	--	323 ± 9.6* 428 ± 3.4	25.9 ± 0.24*	3.0 ± 0.01*
5	-15.7 ± 2.1*	--	--	321 ± 10.8* 421 ± 4.0	30.4 ± 0.11*	3.1 ± 0.03*
8	-14.6 ± 1.9*	--	--	335 ± 13.2* 427 ± 2.2	--	5.5 ± 0.02*

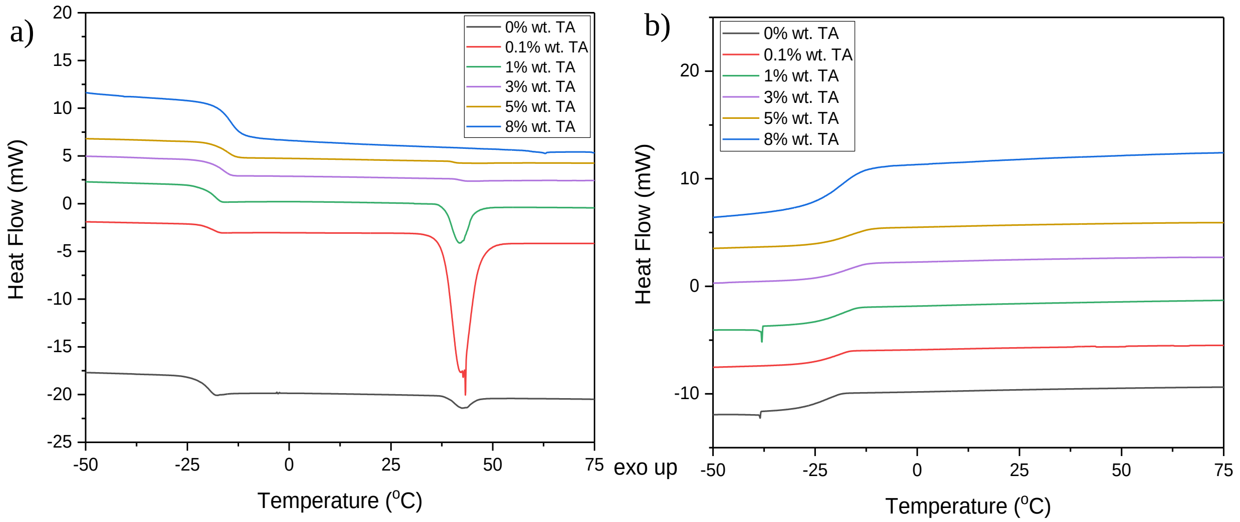

Figure 2.6: DSC of TA-DGEBA composites: a) heat and b) cool

Previous researchers have found that TA and epoxy resin will react at elevated temperature.[32, 43, 44] However, the results from this study further indicate and elaborate on the molecular behaviors between TA and DGEBA previously unexplored in the literature. At low loading levels, DGEBA reacts with TA to functionalize its surface, but the odds of DGEBA-functionalized TA molecules finding additional phenol groups in solution are rare – due to the extreme excess of epoxy groups in the solution. However, at loading levels at or above 1% TA, the molecules in the solution are present in high enough amounts to find each other and react forming a cross-linked network (Figure 2.7). DSC results corroborate this claim, as surface-modified TA molecules in concentrations below 1 wt% TA act as nucleation sites in the solution resulting in higher crystallinity and a larger magnitude to the crystallization peak in the heat curve. Further, samples which are simply surface modified show similar T_g to control samples, whereas samples which are not only surface modified but also crosslinked show significant increases in T_g as compared to the control on DSC. The cross-linked networks largely formed in samples with concentrations of TA at or above 3 wt% TA are more thermally stable than the DGEBA-functionalized TA molecules in solution and degrade at higher temperature – 425°C. The weight fraction of surface modified TA and crosslinked TA in the solution was calculated from the thermogram using the residual mass fractions during the plateau and after the second thermal degradation temperature (

Table 2.1). Due to the broad nature of the degradation peak at 425°C, there is evidenced a broad distribution of crosslink densities throughout the system, with some crosslinks being less dense and degrading below 400°C, while others are denser and degrade near 450°C.

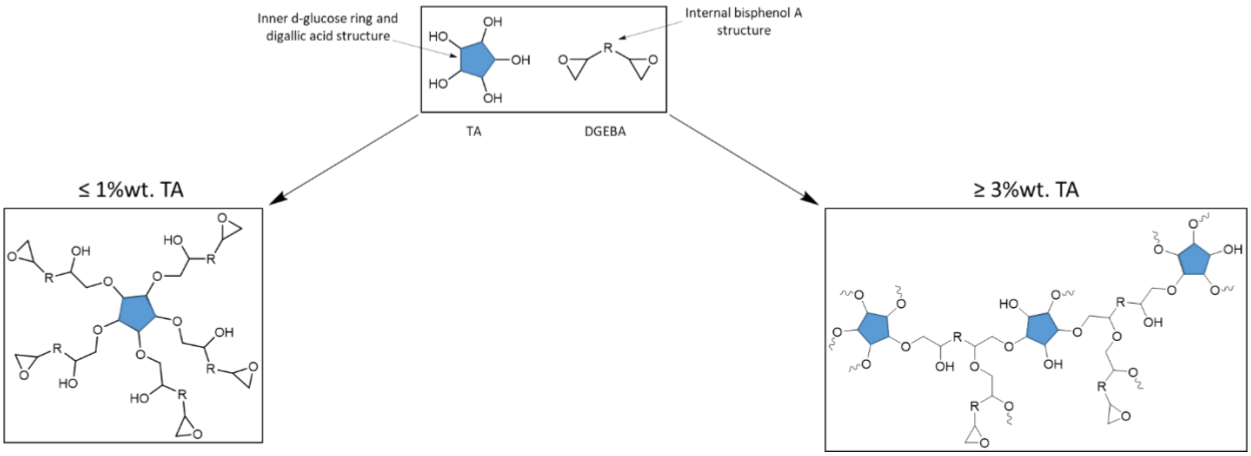

Figure 2.7: Reaction scheme for the concentration dependence of the molecular interactions of TA and DGEBA in solution.

This result is also consistent with UV-Vis data which indicates a fundamental solubility change between samples loaded at or below 1 wt% TA and those loaded at or above 3 wt%. The increase in the presence of agglomerations in the higher-TA loaded samples suggests a non-uniformly reacted composite, with regions of less-reacted and more-reacted being incompatible with each other resulting in micro-phase separation, something not visible to the naked eye, but more easily observed under UV-light where the light is scattered more easily by these agglomerates. Such results have not been seen before in the literature.

2.4.2 Crosslinked Epoxy Thermosets

After hardening the TA-DGEBA pre-polymers using GP2074, the epoxy samples were characterized to determine their mechanical properties (Figure 2.8). At low TA-loading levels (≤ 1 wt% TA), an observable decrease in ultimate strength, stiffness, and work-of-fracture were seen. However, at higher TA loading levels (≥ 3 wt% TA) samples were not found to be significantly different from the control sample. The preliminary explanation for this behavior is that surface-functionalized DGEBA-TA molecules in small concentrations decreased the overall crosslinking density of the sample resulting in a less strong, stiff, and tough thermoset. In order to corroborate these claims, crosslink density of the samples was calculated using dynamic mechanical analysis (DMA) (Table 2.2). Crosslink density was found to change significantly with TA loading. Samples containing low amounts of TA (<1 wt% TA) were found to significantly decrease the crosslinking density of the system as compared to the control. However, loading levels of 3 wt% TA or above significantly increased the crosslinking density. Significant differences were found between all samples ($P<0.05$), with values significantly increasing as TA loading was increased.

Table 2.2: Quantitative Mechanical Analysis of Samples.

	Compressive Modulus (GPa)	Toughness (Work-of-Failure (MJ/m^3)	Ultimate Compressive Strength (MPa)	Glass Transition Temperature (T_g) (°C)	Crosslink Density (10^5 mol/m^3)
0% TA	2.0 ± 0.3	1.0 ± 0.3	190 ± 23	52.5 ± 0.2	2.9 ± 0.01
0.1% TA	1.4 ± 0.4	0.1 ± 0.05*	84 ± 30	52.0 ± 0.6	2.8 ± 0.04*
1% TA	1.6 ± 0.1	0.2 ± 0.1*	110 ± 26	52.7 ± 0.5	2.7 ± 0.01*
3.2% TA	1.6 ± 0.2	0.6 ± 0.3	150 ± 10	56.7 ± 0.4	3.1 ± 0.01*
6% TA	1.5 ± 0.1	0.3 ± 0.02	140 ± 0.2	65.6 ± 0.7	3.0 ± 0.01*
8% TA	1.6 ± 0.1	0.7 ± 0.3	160 ± 3	67.6 ± 0.8	3.5 ± 0.00*

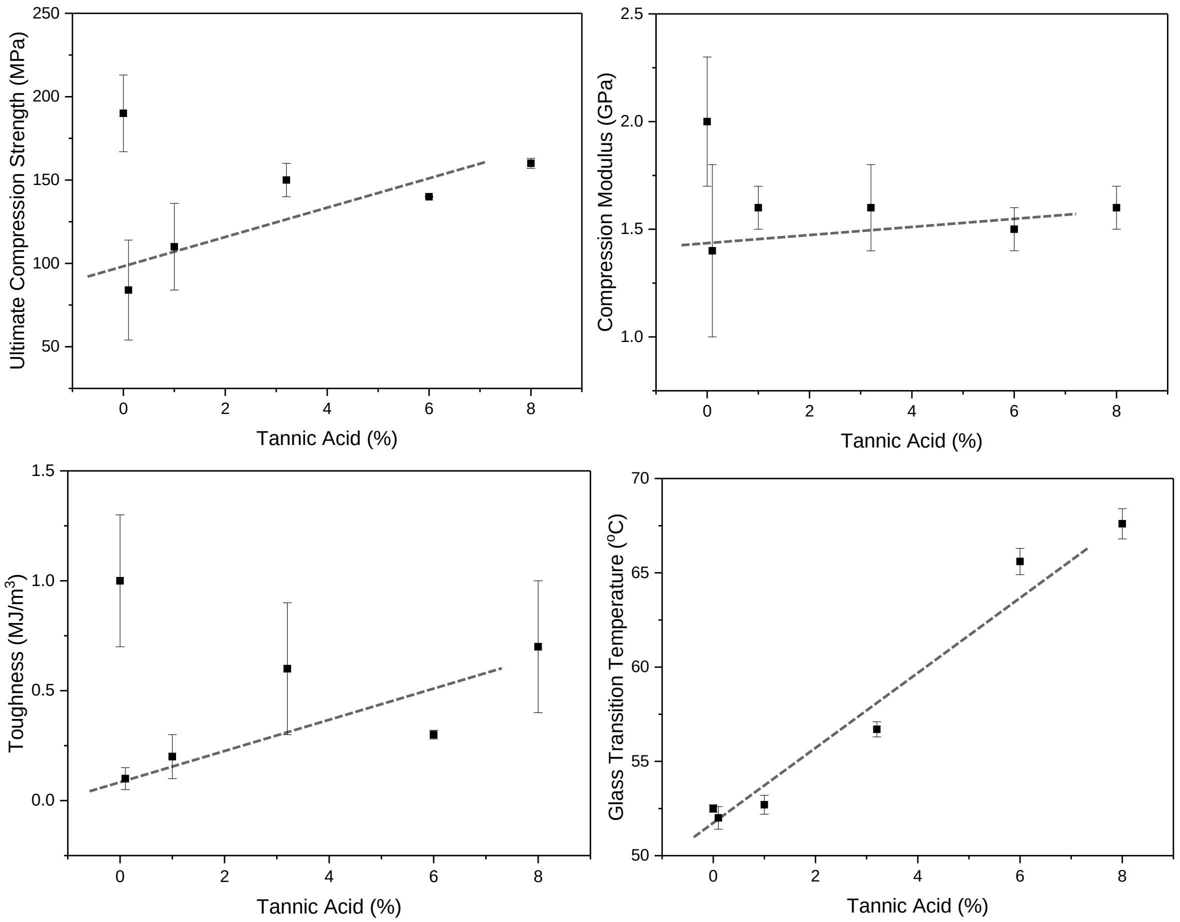

Figure 2.8: Mechanical and thermal testing results of TA-DGEBA-GP2074 composites. Dashed lines added to aid the eye.

DSC was used to characterize the under-cure and the glass transition of the GP2074-hardened samples (Table 2.2 and Figure 2.9). DSC curves showed residual under-cure in all samples during the heat, which disappeared during the cooling. DSC also showed that samples cured with 3 wt% TA or more had significantly increased glass transition temperatures as compared to the control sample. Further, the glass transition temperature was dependent on TA loading into the sample, increasing with TA loading past 1 wt% TA ($p<0.05$). However, at low concentrations the glass transition temperature did not significantly change with the addition of TA to the system.

At low TA-concentrations, the TA molecules are more modified on average per molecule, as evidenced by FTIR. As listed by the manufacturer, GP2074 has a hydroxyl equivalent weight of 104g/eq, whereas TA has a theoretical hydroxyl equivalent weight of 68.04 g/eq. For this reason, it was surprising that the addition of TA to the system would initially decrease the crosslinking density of the system and then increase it. However, the proximity of the three phenol groups which form the galloyl group on the arm make achieving full surface functionalization impossible. Therefore, after the addition of GP2074 and additional heating, TA molecules in the solution cannot react to increase the crosslinking density of the system resulting in no net change in the crosslinking density observed by DMA. However, at higher concentrations of TA (≥3 wt% TA), the molecules randomly crosslink into the system prior to crosslinking with GP2074, thereby providing additional steric limitations to the chemical functionalization of the molecules. It was expected that for this reason TA would increase the crosslinking density of the system. However, the results of this experiment show that the proximity of the phenol groups on TA's surface hinder the reactivity of the individual phenol groups due to steric limitations. Further, at lower loading levels it actually lessens the crosslink density, but does not result in a significant change in the T_g. However, at higher loading levels it increases the crosslink density and significantly increases the T_g.

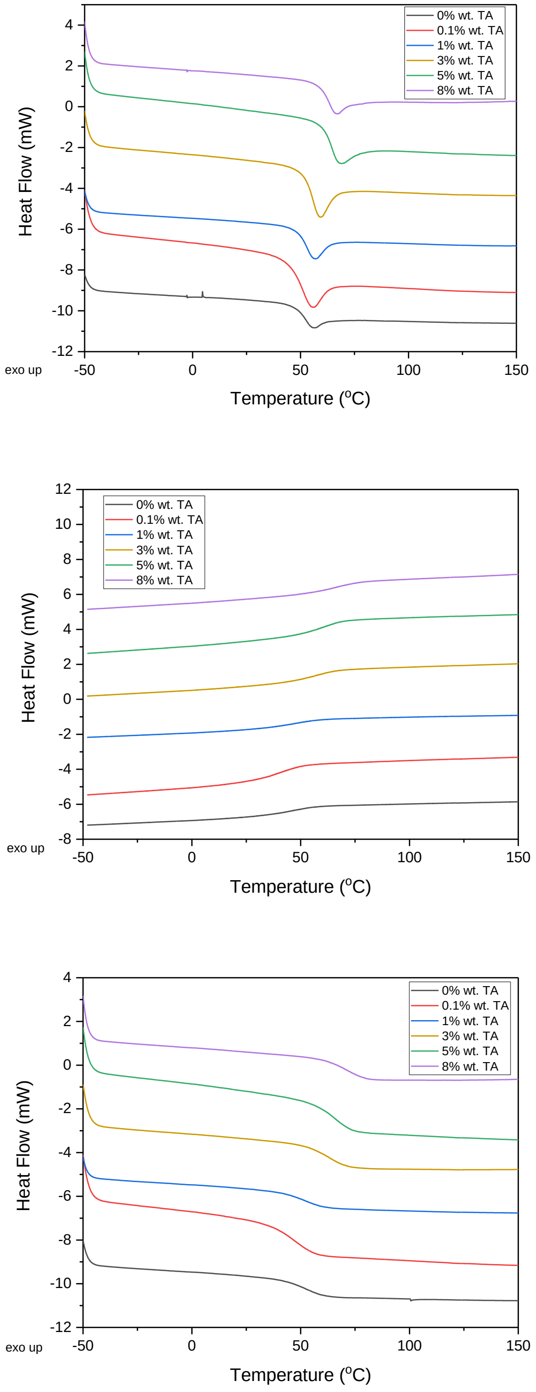

Figure 2.9: DSC of GP2074-hardened TA-DGEBA pre-polymer systems. As can be seen, the glass transition temperature of the samples is dependent upon TA loading.

The GP2074-hardened samples were also characterized using TGA in nitrogen to obtain a preliminary measurement of the FR ability of the composites containing TA (Figure 2.10). Preliminary results show that there is a significant increase to the temperature of thermal degradation of samples loaded at 1 wt% TA or above. However, each sample shows two peaks of thermal degradation, one at 300°C, consistent with the degradation temperature of the surface modified TA molecules as well as both the control TA and DGEBA curves, and a second at 425°C, consistent with the crosslinked TA-DGEBA degradation peak. The magnitude of the derivative weight curve does not correlate with the amount of TA added to the solution at 425°C . Samples of 1 wt% or higher TA were found to have significantly increased T_d as compared to control samples, while 0.1wt% samples did not significantly change as compared to the control samples.

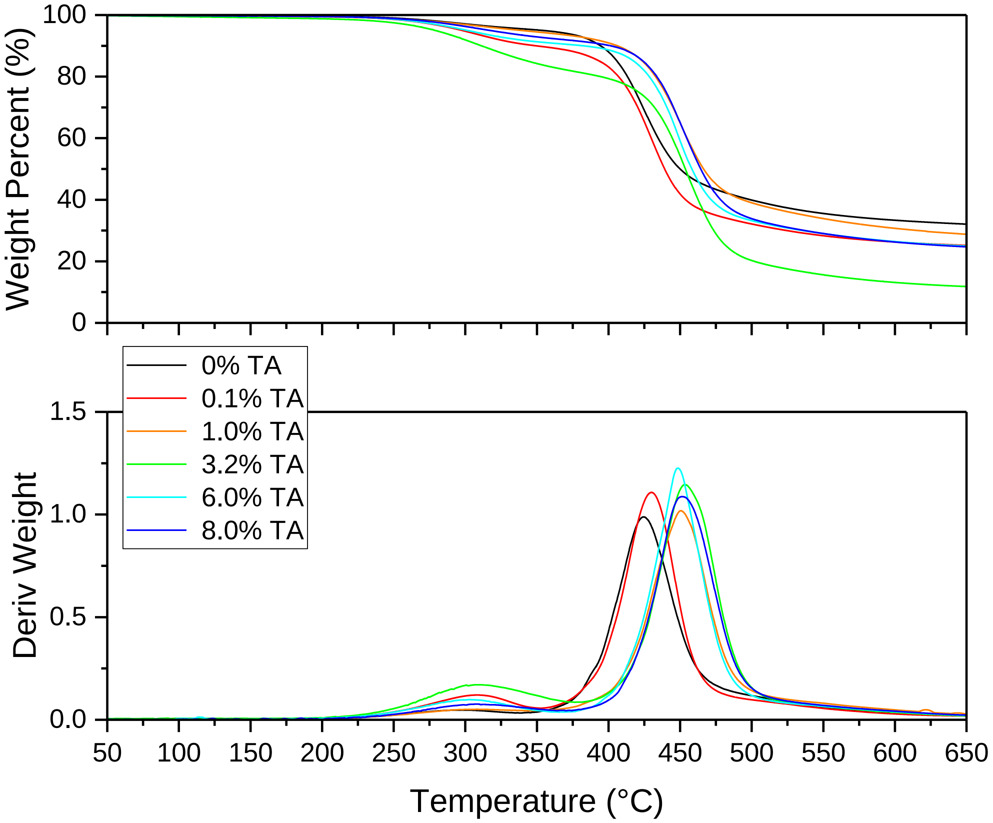

Figure 2.10: TGA of GP2074-hardened TA-DGEBA pre-polymer systems.

Un-hardened TA-DGEBA composites show increased thermal stability, as compared to either control alone. When these composites are hardened with GP2074, the thermal stability of the resulting epoxy is increased only in samples at 1 wt% TA or higher. Surprisingly, samples were not found to have significantly changed remaining char at 600°C as compared to the control samples. The preliminary explanation for this behavior is that adding TA to DGEBA in small amounts increased the thermal stability of the resin because it had reacted into the DGEBA-networks. The data indicates that the surface modified TA molecules, which did not crosslink in the un-hardened samples, are now able to crosslink with the GP2074. The resulting TA-DGEBA-GP2074 network is more thermally stable than just DGEBA-GP2074 networks, resulting in an increased thermal stability. However, GP2074 is unable to fully crosslink the solution using this procedure, resulting in residual, un-reacted, surface modified TA-DGEBA remaining in the crosslinked thermoset, which degrades at lower temperature.

Flame Retardancy Analysis

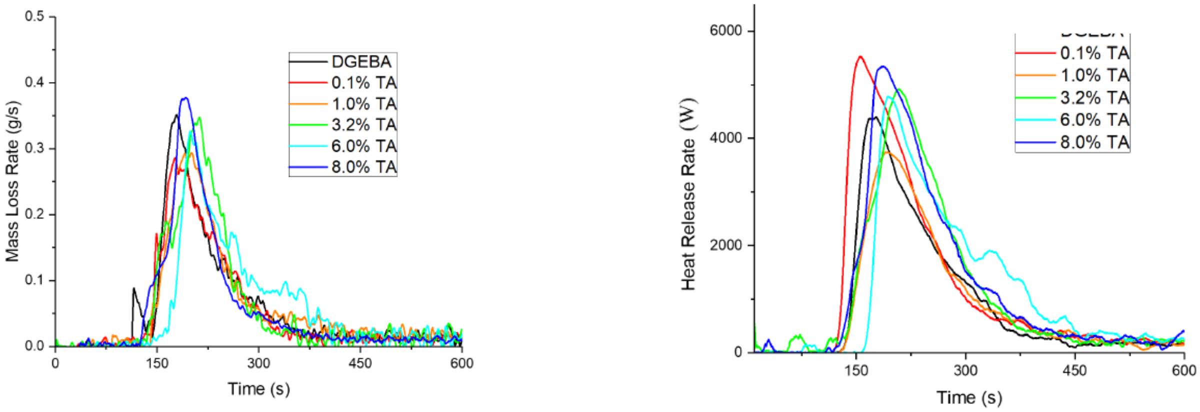

Figure 2.11: MLC of GP2074-hardened TA-DGEBA pre-polymer systems.

To determine the flame retardancy of the GP2074-hardened TA-DGEBA thermosets, epoxy samples were analyzed using mass loss calorimetry (MLC) (Figure 2.11). Results indicate that at low TA loading levels in DGEBA that have been hardened with GP2074, there was no significant change in the peak heat release rate. Surprisingly, in samples containing TA in 3.2 weight percent or higher, the peak heat release rate actually increased and did not correlate with greater TA loading. The time to ignition did not significantly change from sample to sample, and in some cases, decreased with TA loading. The mass loss rate behavior was the same regardless of TA-loading. Past a 1% TA-loading level, the peak of the mass loss rate curve increased significantly as compared to the control but not relative to the amount of TA present in the sample. These results indicate that TA which is surface functionalized with DGEBA is unable to function as a flame retardant once hardened with GP2074. The total mass loss was consistent between all samples; the TA did not increase the amount of the sample remaining after mass loss calorimetry analysis. Samples containing TA showed slightly decreased mass loss during the duration of the test which indicated that in the fire itself, TA can form small amounts of char, but the mass loss was most decreased in the highly TA loaded samples

Although the quantifiable data obtained by mass loss calorimetry shows no statistically significant changes in the peak heat release rate (HRR) and mass loss rate (MLR) of samples containing TA, visually, the samples ignited quite differently. With increased TA loading, the fire propagated slower across the surface of the sample. The samples that had decreased mass loss and delayed fire propagation across the surface were also the samples that showed phase separation and clumping when analyzed with optical microscopy. The initial explanation is that unmodified TA was available in the system to delay the propagation of the fire. It is also of note to mention that samples containing TA did not show significantly increased char formation by mass but did show an increase in intumescent behavior (Figure 2.12). This result indicates that the presence of TA does not noticeably increase or decrease the ignitability of the samples, which matches the data for the time o ignition measured by mass loss calorimetry.

0% TA top and side view **3.2% TA top and side view** **8% TA top and side view**

Figure 2.12: Resulting chars from MLC test.

The preliminary explanation for this behavior is that in higher TA-concentrations, the molecules have more un-reacted -OH groups per molecule, resulting in a decreased HRR and MLR as compared to low-TA loaded systems due to the increased FR ability. To circumvent compatibility limitations which have been found to significantly impact the mechanical properties of the resultant polymers, the surface of TA molecules was modified to better match the epoxy resin and therefore increase dispersibility. However, the results of this study suggest that the ability for TA to retard the spread of a fire is directly proportional to the presence of the phenol groups on the surface of the molecule – the very thing limiting compatibility. Removing the flame retardant –OH groups from the surface of the molecule did not allow for the TA molecules to retard the spread of the fire significantly, something not seen before in literature for this molecule.

Highly surface functionalized molecules that were not pre-reacted into the system (≤1 wt% TA) showed no significant differences in the resulting flame retardancy nor resulting intumescent behavior as compared to control samples. This result was expected as TA was loaded in very small amounts so little resulting material changes should be observed. However, as TA was loaded in higher amounts (3wt% or higher) the resulting HRR was found to increase. This indicated that even residual phenol groups in the higher wt% TA systems were not readily available to slow the propagation of the fire at the flame front within the pre-reacted thermoset. The initial explanation for this behavior is that although phenol degradation happens at lower temperature in the TGA, the flame front is likely at a temperature at which oxidation, crosslinking, and phenol degradation are occurring simultaneously. Perhaps crosslinking at the flame front in higher TA-loaded samples is hiding un-reacted phenol groups in the sample. TGA results indicated that crosslinked samples had less readily available residual phenol groups. This was evidenced by the increased temperature of thermal degradation in samples containing 3 wt% or more TA. As crosslinking occurs and pushes the flame front up-and-away from the bottom of the fixture, less-readily available phenol groups could get left behind the flame front and thus be unable to retard the spread of the fire where it will be most impactful.

These results also suggest that it is not the phenol groups that affect the molecule's ability to increase a polymer's intumescent behavior. Instead, it could be that the internal structure (d-glucose ring, phenyl rings of the gallic acid groups) of the molecule alone is what results in intumescent behavior. Upon thermal degradation, TA becomes oxidized and crosslinks into the polymer network. Simultaneously, previous research suggests that the thermal degradation of TA releases CO_2, CO, and H_2O gas into the atmosphere.[25] Our work corroborates these claims. The disappearance of phenol groups due to surface functionalization or crosslinking did not significantly affect the char forming ability of the molecule but did directly impact the ability of the molecule to decrease the HRR after flame propagation. The combination of crosslinking and release of gas causes the intumescent behavior seen in this work. Using this knowledge, a more flame retardant and intumescent TA-based additive for epoxy systems may be engineered. It is important to understand that the compatibility limitations of TA in epoxy causes decreased mechanical properties in the resulting solubility. However, simply surface modifying the molecule to circumvent these compatibility limitations will result in a purely intumescent material with no significant changes to the HRR.

2.5 Conclusion

Currently used industrial flame-retardant additives have unintended impacts on both the environment and human health, and there is significant industrial demand for biologically-sourced additives to replace these more toxic compounds. Currently, one of the major limitations to many of these biologically sourced compounds is poor compatibility between the additive and the polymer matrix, and this is especially the case for TA in epoxy. Using high temperature processing techniques, up to 8 wt% TA was dispersed in epoxy resin with good compatibility, and its intumescenct behavior was studied. The results from this study indicate that adding TA to a DGEBA epoxy resin can not only serve to increase the intumescent behavior of the polymer without significantly impacting the mechanical properties of the polymer, but that it can also decrease the propensity for epoxy resin to crystallize in transit. Both results indicate that TA has the potential to serve as a biologically sourced, economical replacement to currently available intumescent epoxy additives.

2.6 Acknowledgments

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2.7 References

1. Bukowski, R.; Waterman, T.; Christian, W., Detector sensitivity and siting requirements for dwelling [Final Report]. Bukowski, R., Ed. 1975; pp 337P-337P.

2. Bukowski, R.; Peacock, R.; Averill, J.; Cleary, T.; Bryner, N.; Walton, W.; Reneke, P.; Kuligowski, E. *Performance of Home Smoke Alarms: Analysis of the Reponse of Several Available Technologies in Residential Fire Settings*; Washington, D.C., USA, 2007.

3. Rossen, J.; Davis, J. Newer homes and furniture burn faster, giving you less time to escape a fire. https://www.today.com/home/newer-homes-furniture-burn-faster-giving-you-less-time-escape-t65826.

4. Callister, W. D., *Materials Science and Engineering*. 9th edition, SI version.. ed.; Wiley Textbooks.

5. Peng, L.; Deng, Y.; Yi, P.; Lai, X., Micro hot embossing of thermoplastic polymers: a review. *Journal of Micromechanics and Microengineering* **2014,** *24*, 1-23.

6. Chen, Z., Multi-level modeling of woven glass/epoxy composite for multilayer printed circuit board applications. *International Journal of Solids and Structures* **2014,** *51* (21-22), 3679--3688.

7. Haugan, E.; Per Dalsjo, P., Characterization of the material properties of two FR4 printed circuit board laminates. FFI Rapport, 2014.

8. Composite Adhesives Market by Resin (Epoxy, Polyurethane), Component (One-Component, Two-Component), Application (Automotive & Transportation, Marine, Aerospace, Wind Energy), and Region - Global Forecast to 2022. (accessed October 4).

9. Kuruppalil, Z. In *Green Plastics: An Emerging Alternative for Petroleum Based Plastics?*, IAJC-ASEE International Conference, Hartford, Connecticut, Hartford, Connecticut, 2011.

10. Kuruppalil, Z. In *Plastics packaging: the challenge of going green*, The First International Conference on Green and Sustainable Technology, University of North Carolina A&T, University of North Carolina A&T, 2011.

11. Li, Y.; Xiao, F.; Moon, K.; Wong, C., Novel curing agent for lead-free electronics: Amino acid. *Journal of Polymer Science Part a-Polymer Chemistry* **2006,** *44* (2), 1020-1027.

12. Baroncini, E.; Yadav, S.; Palmese, G.; Stanzione, J., Recent advances in bio-based epoxy resins and bio-based epoxy curing agents. *Journal of Applied Polymer Science* **2016,** *133* (45).

13. De Poortere, M.; Schonbach, C.; Simonson, M., The fire safety of TV set enclosure materials, a survey of European statistics. *Fire and Materials* **2000,** *24* (1), 53-60.

14. Waaijers, S. L.; Kong, D.; Hendriks, H. S.; De Wit, C. A.; Cousins, I. T.; Westerink, R. H. S.; Leonards, P. E. G.; Kraak, M. H. S.; Admiraal, W.; De Voogt, P.; Parsons, J. R., Persistence, bioaccumulation, and toxicity of halogen-free flame retardants. *Reviews of Environmental Contamination and Toxicology* **2013,** *222*, 1-71.

15. Liu, Y., The Decomposition of Bisphenol A Diglycidyl Ether/Alicyclic Amine Hardened Networks in Near-critical Water. *Polymers & Polymer Composites* **2012,** *20* (9), 809-816.

16. Cohen, J. L.; Van Aartsen, J. J., The hydrolytic degradation of polyurethanes. *Journal of Polymer Science: Polymer Symposia* **1973,** *42* (3), 1325-1338.

17. Covaci, A.; Harrad, S.; Abdallah, M. A. E.; Ali, N.; Law, R. J.; Herzke, D.; de Wit, C. A., Novel brominated flame retardants: A review of their analysis, environmental fate and behaviour. *Environment International* **2011,** *37* (2), 532-556.

18. Weil, E. D., Fire-protective and flame-retardant coatings - a state-of-the-art review.(Report). *Journal of Fire Sciences* **2011,** *29* (3), 259-296.

19. Weil, E. D., *Flame retardants for plastics and textiles : practical applications*. Place of publication not identified Hanser Publishers: 2016.

20. Andreas S., Flame retardants in indoor air at an electronics recycling plant and at other work environments. *Environmental Science & Technology* **2001,** *35* (3), 448.

21. Darnerud, P. O.; Aune, M.; Larsson, L.; Lignell, S.; Mutshatshi, T.; Okonkwo, J.; Botha, B.; Agyei, N., Levels of brominated flame retardants and other pesistent organic pollutants in breast milk samples from Limpopo province, South Africa. *Science of the Total Environment* **2011,** *409* (19), 4048-4053.

22. Kandola, B. K.; Horrocks, A. R.; Price, D.; Coleman, G. V., Flame-Retardant Treatments of Cellulose and Their Influence on the Mechanism of Cellulose Pyrolysis. *Journal of Macromolecular Science, Part C* **1996,** *36* (4), 721-794.

23. Alongi, J.; Carletto, R. A.; Di Blasio, A.; Carosio, F.; Bosco, F.; Malucelli, G., DNA: a novel, green, natural flame retardant and suppressant for cotton. *J. Mater. Chem. A* **2013,** *1* (15), 4779-4785.

24. Visakh, P. M., *Flame Retardants Polymer Blends, Composites and Nanocomposites*. Cham : Springer International Publishing : Imprint: Springer: 2015.

25. Xia, Z.; Singh, A.; Kiratitanavit, W.; Mosurkal, R.; Kumar, J.; Nagarajan, R., Unraveling the mechanism of thermal and thermo-oxidative degradation of tannic acid. *Thermochimica Acta* **2015,** *605*, 77--85.

26. Arbenz, A.; Avrous, L., Chemical modification of tannins to elaborate aromatic biobased macromolecular architectures. *Green Chem.* **2015,** *17* (5), 2626-2646.

27. Chaoqun, Z.; Aaron, M.; Merid, H.; Garret, M.; C, G. J., Nanocoating of starch and clay that reduces the flammability of polyurethane foam. *Green Materials* **2017,** *5* (4), 182-186.

28. Chen, H.-B.; Wang, Y.-Z.; Sánchez-Soto, M.; Schiraldi, D. A., Low flammability, foam-like materials based on ammonium alginate and sodium montmorillonite clay. *Polymer* **2012,** *53* (25), 5825-5831.

29. Pascault, J.-P. a. W. R. J. J., Chap 1. General Concepts about Epoxy Polymers in Epoxy Polymers. *Epoxy Polymers: New Materials and Innovation* **2010**, 4.

30. Soares, B. G. a. L. S., *Handbook of Epoxy Blends*. 2017; p 1--39.

31. Mendis, G.; Weiss, S.; Korey, M.; Boardman, C.; Dietenberger, M.; Youngblood, J.; Howarter, J., Phosphorylated Lignin as a Halogen-Free Flame Retardant Additive for Epoxy Composites. *Green Materials* **2016,** *4* (4).

32. Korey, M.; Mendis, G. P.; Youngblood, J. P.; Howarter, J. A., Tannic acid: A sustainable crosslinking agent for high glass transition epoxy materials. *Journal of Polymer Science Part A: Polymer Chemistry* **2018,** *56* (13), 1468-1480.

33. Grigsby, W. J.; Kadla, J. F., Evaluating Poly(lactic acid) Fiber Reinforcement with Modified Tannins. *Macromolecular Materials and Engineering* **2014,** *299* (3), 368-378.

34. Burkinshaw, S. M.; Bahojb-Allafan, B., The development of a metal-free, tannic acid-based aftertreatment for nylon 6,6 dyed with acid dyes. Part 4: tannic acid. *Dyes and Pigments* **2004,** *62* (2), 159-172.

35. Society of Plastics, E., *Tannic Acid: A Bio-Based Intumescent Char-Forming Additive for Nylon 6*. Society of Plastics Engineers: 2016; p 1-5.

36. Amaral-Labat, G.; Szczurek, A.; Fierro, V.; Pizzi, A.; Celzard, A., Systematic studies of tannin–formaldehyde aerogels: preparation and properties. *Science and Technology of Advanced Materials* **2013,** *14* (1).

37. Liu, M.; Cai, C.; Li, J.; Zhao, J.; Teng, W.; Liu, R., Stöber synthesis of tannic acid–formaldehyde resin polymer spheres and their derived carbon nanospheres and nanocomposites for oxygen reduction reaction. *Journal of Colloid And Interface Science* **2018,** *528*, 1-9.

38. Ontiveros-Ortega, A.; Espinosa-Jiménez, M.; Chibowski, E.; González-Caballero, F., Effect of Tannic Acid on the Surface Free Energy of Polyester Dyed with a Cationic Dye. *Journal of Colloid And Interface Science* **1998,** *199* (1), 99-104.

39. Thébault, M.; Pizzi, A.; Essawy, H. A.; Barhoum, A.; Van Assche, G., Isocyanate free condensed tannin-based polyurethanes. *European Polymer Journal* **2015,** *67* (C), 513-526.

40. Thébault, M.; Pizzi, A.; Santiago-Medina, F. J.; Al-Marzouki, F. M.; Abdalla, S., Isocyanate-free polyurethanes by coreaction of condensed tannins with aminated tannins. *Journal of Renewable Materials* **2017,** *5* (1), 21-29.

41. Jaime-Anne, E.; Warren, J. G.; Cole, L.; James, H. B., Esterification of Condensed Tannins and Their Impact on the Properties of Poly(Lactic Acid). *Polymers* **2013,** *5* (2), 344-360.

42. Fei, X.; Zhao, F.; Wei, W.; Luo, J.; Chen, M.; Liu, X., Tannic Acid as a Bio-Based Modifier of Epoxy/Anhydride Thermosets. *Polymers* **2016,** *8* (9).

43. Shibata, M.; Nakai, K., Preparation and Properties of Biocomposites Composed of Bio-Based Epoxy Resin, Tannic Acid, and Microfibrillated Cellulose. *Journal of Polymer Science Part B-Polymer Physics* **2010,** *48* (4), 425-433.

44. Shibata, M.; Teramoto, N.; Makino, K., Preparation and Properties of Biocomposites Composed of Epoxidized Soybean Oil, Tannic Acid, and Microfibrillated Cellulose. *Journal of Applied Polymer Science* **2011,** *120* (1), 273-278.

3. TANNIC ACID: A SUSTAINABLE CROSSLINKING AGENT FOR HIGH GLASS TRANSITION EPOXY MATERIALS

This chapter is based upon work that was previously published *Journal of Polymer Science: Part A.*

Korey, M.; Mendis, G. P.; Youngblood, J. P.; Howarter, J. A., Tannic acid: A sustainable crosslinking agent for high glass transition epoxy materials. *Journal of Polymer Science Part A: Polymer Chemistry* **2018,** *56* (13), 1468-1480. DOI: https://doi.org/10.1002/pola.29028

For this chapter, I wrote the text and performed all of the testing myself in collaboration with the co-authors of this work. However, I was the one who performed all the sample testing and analysis with intellectual input from other collaborators.

3.1 Abstract

Epoxy thermosets have revolutionized the coating, adhesive, and composite industries but the chemicals from which they are synthesized have significant effects on the environment and human health not only pre-cure but also after crosslinking has occurred. In this study, we propose tannic acid (TA) as an alternative epoxy hardening agent for commercially available epoxy resin, the diglycidyl ether of bisphenol A (DGEBA). The resulting thermosets were characterized by Fourier transform infrared spectroscopy, optical microscopy, dynamic mechanical analysis, differential scanning calorimetry, and thermogravimetric analysis. The results from this study showed that at temperatures above 100ºC the compatibility of TA in DGEBA was significantly increased for loading levels up to 37% weight of TA in DGEBA, something that has not been seen before in literature. It was also discovered that at high loading levels, the resulting materials had glass transition temperatures at and above 200ºC. The resulting material was proposed as a more sustainable alternative to amine or acid hardened epoxy thermosets and was particularly useful in high-temperature applications.

3.2 Introduction

In 2015 global plastics demand exceeded 300 million tons, and this value is growing steadily.[1,2] Since 1980, the plastics industry has grown at an annual, average rate of 3.4 percent, with US plastics companies alone employing over 1 million workers and providing nearly $379 billion in annual shipments.[1,2] Plastics are used in a variety of applications due to their low density, the ease with which they are processed, and low cost.[3] Two major drawbacks to the prevalence of plastics is that the source for most commercial plastics is petroleum and 40% of the total consumption of plastics is short-term use, which, in tandem, mean that producers are using non-renewable resources to make a product that will be used once or twice and then put into waste.[1-3] Most plastics products that are used by consumers are non-compostable and non-biodegradable and thus end up persisting in the waste streams, like landfills. Rapid, often unplanned, urbanization can often leave municipalities overwhelmed and unprepared for the disposal of increasing amounts of waste.[3] Further, separation of the constituent chemicals of plastics is often quite challenging, exceedingly expensive, and can require a significant amount of energy; thus, there is little drive to recycle these products industrially.[1,2] Therefore, when considering sustainability, one of the most commonly targeted materials is plastics.[1-3]

Polymers can be designed to have properties desirable to a multitude of applications. Thermoplastic polymers, such as nylon, polyethylene, or polyvinyl chloride, are found in applications such as piping, food packaging, insulation, and clothing.[4] Thermoset polymers, such as epoxies and polyurethanes, are often found in coatings, structural applications, and adhesives.[5-7] There has been a significant amount of research to increase the sustainability of thermoplastic polymers, in particular, with regard to food packaging applications which currently demand the largest market share of the plastics industry.[1,2] Researchers have found ways to sustainably source a variety of thermoplastics including polyhydroxyalkanoate,[8-12] polylactic acid,[12,13] poly(butylene succinate),[14,15] poly(trimethylene terephthalate),[12,13,16] polyethylene,[13,17,18] polypropylene,[12,19-21] polyethylene terephthalate,[12,22,23] and others.[12] There has even been a significant amount of work in the area of thermoplastic elastomers including triblock copolymers consisting of bio-derived poly(lactide) sourced from corn and sugar beets reacted with a variety of end groups including poly(menthide) synthesized from (-)-menthol found in mint leaves, as well as bio-sourced poly(ethylene glycol), poly(isoprene), and poly(ricinoleic acid).[24-29]

There is also a significant amount of research on the development of sustainable thermoset polymers; in particular, with regard to the adhesives and coatings industries. Previous researchers have developed sustainably-sourced acrylics using acrylic acid and methacrylic acid soured from biomass.[30,31] Renewable, unsaturated polyester thermosets have also been synthesized using 1,2-propylene glycol sourced from triglycerides and sugars.[32-34] Bio-inspired urethanes have been synthesized including bio-sourced hexamethylene diisocyanate and isophoronediisocyanate.[35-38] Some of the above chemical synthesis pathways have been patented and used industrially for the preparation of thermoset polymers that are biologically derived. However, while there is also a significant amount of work being done in the area of epoxy thermoset sustainability, there are very few industrially-viable biologically-sourced epoxy monomers currently used.

Due to their excellent mechanical strength, good thermal, electrical, and chemical resistance and superb adhesion to many substrates, epoxy based polymers are considered one of the most versatile and important thermosetting polymers.[39,40] Epoxy polymers are used in a wide range of applications including coatings,[41] adhesives,[42] structural composites,[43] insulating materials,[44] and in components of electronics.[5,6] Global epoxy market demand is expected to increase at a compound annual growth rate of 7.9% from 2016 to 2020, with an expected annual demand of 2,115.6 ktons in the coatings sector alone by 2024.[7,45,46] An epoxy thermoset is often made of two constituent chemicals: an epoxy resin and a hardening agent, which react to form a molecular-level, dense, covalent chemical network. For many applications for epoxy polymers, the material is subject to high-temperature environments after the initial crosslinking procedure. Because of this, not only do these materials need to be stable in high-temperature environments but they also need to maintain their stiffness at higher temperature. Currently, after initial synthesis, several electronic components are soldered to epoxy circuit boards at temperatures close to 180°C although their glass transition temperatures (T_g) tend to be closer to 140°C.[6] Repeatedly exposing these epoxy thermosets to temperatures significantly above their T_gs leads to a localized softening of the thermoset during the soldering process. This behavior not only greatly hinders the process overall but also leads to reduced T_g and temperature of thermal decomposition (T_d) of the bulk material.[47] Because of this reduction in thermal stability and thermomechanical properties, the T_g and T_d are often used when determining the application in which an epoxy material can be used. Epoxy materials with T_gs above 160 ºC are considered high T_g epoxy materials in industry.[48,49]Enhancing both T_g and T_d can greatly increase the variety and diversity of applications in which epoxy materials can be utilized.

While the properties of epoxy thermosets are desirable, two of the main concerns with their use are: 1) the precursor chemicals are industrially synthesized from non-renewable petroleum resources[40,50] and 2) the toxicity of the precursor chemicals is well known, especially for hardeners used in high temperature applications.[51,52] Even for cured epoxy resins, toxicity cannot be avoided because of the possibility of incomplete consumption of curing agents and the subsequent hazards introduced by the residue.[40] Despite the known health and environmental impacts of all commercially available curing agents of epoxy resins, such as polyamines,[53,54] acid anhydrides,[40,54] and sulfur-based hardeners,[55] there are currently no biologically-sourced, non-toxic high glass transition (T_g) epoxy hardening agents that are used industrially.[40]

A variety of biologically-sourced chemicals have been researched to alleviate these concerns in epoxy systems. In order to replace currently used amine hardening agents, researchers have functionalized grapeseed, cardanol, and furans with reactive amine groups.[56-59] In order to replace currently used anhydride hardening agents, researchers have developed anhydride-functionalized terpene.[60] Unmodified chemicals have also been explored to avoid these concerns including cardanol, amino acids, citric acid and other acids, and rosins.[57,61-64] Commercialization of these biologically-sourced, non-toxic compounds is often inhibited by their complex synthesis and isolation mechanisms. Furthermore, their T_g values are too low for high T_g applications.[65]

Another biologically-sourced, non-toxic compound is tannic acid (TA) (Figure 3.1). TA is a polyphenolic compound that is found in nuts, galls, seeds, and tree bark that is generally regarded as safe (GRAS) and has been used as a food additive.[66,67] The chemical formula for TA is usually given as $C_{76}H_{52}O_{46}$ but it often contains a mixture of related compounds based mainly on the glucose ester of gallic acid.[68] It is also currently industrially produced for a variety of applications including for the tanning of leather[69] and as an additive for antihistamine and antitussive products.[70] TA is an inexpensive chemical and can be purchased for similar costs to currently available industrial high T_g epoxy hardeners, as TA and 4,4'-Diaminodiphenyl sulfone cost $36 and $35 per kilogram.[71-73] Previous researchers have determined that under the right conditions, the catecholic -OH groups on TA are capable of reaction with oxirane rings making it potentially chemically suitable to act as a chemical hardener for epoxy.[68,74] The use of TA as a crosslinking agent in epoxy thermosets is very limited, but TA potentially has 25 gallol hydroxyl groups that are capable of crosslinking into an epoxy network.

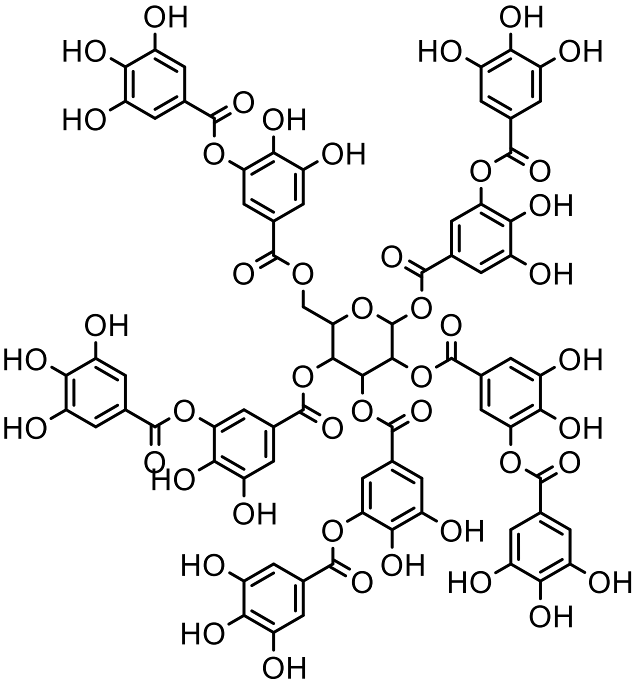

Figure 3.1: Idealized molecular structure for tannic acid (TA).

TA has been studied for use as a crosslinking agent for bio-based epoxy systems, but the resulting T_gs were below 100°C even with additional chemical functionalization and curing at 200°C, limiting their use to low-temperature applications.[68,74] Previous researchers have pursued TA as a toughening agent for the diglycidylether of bisphenol A (DGEBA) (Figure 3.2) in anhydride-hardened epoxies, but explored loading levels between 0.5% and 2% weight TA in epoxy and did not achieve glass transition temperatures above 151ºC.[75] Other researchers have used pyridine-catalyzed esterification as a chemical modification to increase compatibility of TA in epoxy and used an anhydride hardening agent as well, but compatibility limitations again prevented loading levels above 2% weight and resulting T_g values at all loading levels were lower than 145ºC.[76] To the best of our knowledge, TA has never been used as a high T_g epoxy crosslinking agent and has never been explored as the lone crosslinking agent for currently commercially available epoxy resins mainly because hydrophilic TA has very limited compatibility in the hydrophobic epoxy resin even at elevated temperatures like 60ºC. Compatibility at temperatures above this has not been explored in the literature. However, because of its comparably low cost and the fact that it is already industrially isolated, if compatibility limitations can be circumvented TA has the potential to serve as an alternative to other high T_g epoxy hardeners that are biologically-sourced and industrially viable.[69]

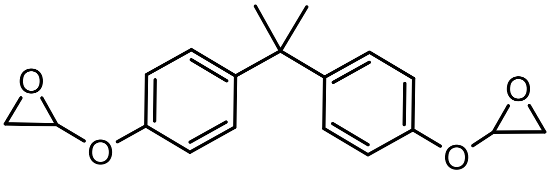

Figure 3.2: The molecular structure of the diglycidyl ether of bisphenol A (DGEBA).

The purpose of this study was to use TA as a more sustainably-sourced, alternative crosslinking agent for commercially available epoxy resin (DGEBA) and to evaluate the thermal stability and thermomechanical properties of the resulting cured thermoset material. The comparative phenolic epoxy hardener sample for this study was chosen to be GP2074 novolac resin, a commercially available phenolic epoxy hardening agent, provided by Georgia Pacific. GP2074 has a recorded LD50 value of 317 mg/kg in rats with a high bioaccumulative potential; conversely, TA has a recorded LD50 value of 2260 mg/kg in rats and is GRAS making it considerably less toxic.[77-79] The resulting thermal stability and thermomechanical properties of the material were tunable to the amount of TA loaded into the sample. The results from this processing method indicated that TA was an industrially available, biologically-sourced epoxy hardening agent for producing a high-T_d and T_g epoxy materials with a price that can compete with currently used, more dangerous/toxic hardening agents. The resulting epoxy showed signs that it would be applicable in a wide-variety of higher-temperature and high-load bearing applications, and could potentially alleviate toxicity issues for humans and the environment faced by the epoxy industry.

3.3 Experimental

3.3.1 Materials:

TA was purchased from Sigma Aldrich (St. Louis, MO, USA). EPON 825 (DGEBA) resin was purchased from Hexion, Inc. (Louisville, KY, USA). Mold Max 60 silicone precursor and initiator – parts A and B - were purchased from Smooth-On, Inc. (Macungie, PA, USA). GP 2074 novolac resin was received from Georgia Pacific (Atlanta, GA, USA). 20mL borosilicate scintillation vials were purchased from Thermo Fisher Scientific (Waltham, MA, USA). Rubber septa were purchased from Thomas Scientific, Inc. (Swedesboro, NJ, USA). 18 gauge needles were purchased from Becton Dickinson (Plainfield, IN, USA).

3.3.2 Silicone Mold Preparation:

The silicone molds were prepared using a procedure described elsewhere.[80] 100 parts of silicone precursor were mixed with 3 parts by weight tin initiator for 2 minutes using a DAC 400 Speedmixer from (FlackTek Inc., Landrum, SC, USA). A negative mold of polyethylene was purchased (TA Instruments, Newcastle, DE, USA) with required dimensions for analysis (5.5 cm x 1.2 cm x 0.35 cm) and this was secured to a glass base. 700 g of mixed silicone were poured on top of this setup, and a weight was placed on top to ensure a level base for the silicone mold. Samples sat for 24 hours at room temperature to cure. The silicone mold was then removed from the apparatus and placed into an oven at 150 °C for epoxy preparation.

3.3.3 Epoxy Sample Preparation:

GP2056 novolac resin was received in large chunks which were too large to properly disperse into DGEBA resin. 50g of sample was placed into a 250mL plastic ball mill container, and alumina milling media was added until the container was half-full. Samples were then ball-milled overnight. TA powder and GP2056 were separately sifted to remove aggregates larger than 106 µm and then each were dried for 30 minutes in an oven at 100 °C to remove coordinated water molecules from the powders. The required weight of DGEBA was added to a scintillation vial and was heated to 60 °C in a sandbath for 15 minutes to reduce the viscosity of the solution and allow for better mixing. TA was added to DGEBA at various molar ratios of the galloyl hydroxyl on TA and the epoxy ring (Table 3.1). Samples of a 0.5:1, 0.66:1, 1:1, and 1.5:1 molar ratio of galloyl group on TA to epoxy group (samples 0.5, 0.66, 1.0, and 1.5 respectively) on DGEBA were prepared. For comparative purposes, an additional sample was prepared using the GP 2074 novolac resin at a 1 to 1 molar ratio of phenol to epoxy using the provided weight per epoxide provided by Georgia Pacific (107 g/eq). The recorded molecular weight of TA (1701 g/mol), idealized number of galloyl groups in the structure (25 galloyl/TA), and the weight per epoxide of DGEBA (175 g/eq) were used for these calculations. TA/DGEBA composites and the comparative novolac sample were mixed in the sandbath at 60 °C for 15 minutes. During this time, samples were isolated from environmental oxygen by sealing the reaction using a rubber septum. Nitrogen was fed into the scintillation vial using a needle which was attached to a nitrogen line and used to pierced through the rubber septum. An additional needle was pierced through for outlet nitrogen gas and was left open to atmosphere. After mixing, the scintillation vial was removed and placed into a second sandbath at 150 °C and reconnected to the nitrogen line. The samples were allowed to heat to this temperature for 10 minutes. Once the composites reached 150 °C, the samples were mixed for 50 minutes until the solution browned and no visible clumps were observed. The silicone mold was heated to 150 °C in the oven before sample fabrication. Composites were then poured into the hot silicone mold. The silicone mold, now containing the composite, was placed into an oven at 150 °C, heated at a heating rate of 5°C per minute until it reached 175 °C and then held for 4 hours. Samples were then removed from the oven and allowed to cool overnight to room temperature.

Table 3.1: Samples were prepared by mixing TA and DGEBA in a variety of molar ratios of phenol to oxirane ring.

Sample Label	Wt.% TA added (%)	Molar Ratio of Phenol to Epoxy Group
0.5	16.7	0.5 : 1
0.66	21.0	0.66 : 1
1	28.6	1: 1
1.5	37.4	1.5: 1

3.3.4 Epoxy Sample Characterization:

Thermogravimetric analysis (TGA) was performed with a Q50 thermogravimetric analyser (TA Instruments, Newcastle, DE, USA). Samples were prepared for TGA analysis by shaving off 20±1.3 mg of sample from epoxy bars. Experiments were performed in nitrogen with a 50 mL/min flow rate using a 20 °C/min heating rate from 30 °C to 800 °C. Three epoxy samples were run at each concentration and results were averaged. T_d was determined by finding the peak of the mass loss rate curve using Universal Analysis (TA Instruments, Newcastle, DE, USA) and averaging the temperature values at this point. Remaining char values were calculated by measuring the weight fraction of the sample using Universal Analysis (TA Instruments, Newcastle, DE, USA) at the completion of the TGA test (800 °C) and then averaging the weight fraction values at this point.

Attenuated total reflectance (ATR) Fourier transform infrared (FTIR) spectroscopy was performed using a PerkinElmer Spectrum 100 FTIR Spectrometer (PerkinElmer, Seer Green, Beaconsfield, UK) outfitted using a zinc selenide (ZnSe) crystal. Samples were scanned from 650 cm^{-1} to 4000 cm^{-1} in transmissive mode. EPON 825 was heated at 400 °C for 1 hour in nitrogen atmosphere. Control EPON 825 samples and TA samples was run through the sample preparation method as described for the TA/DGEBA composites but were allowed to cool to room temperature after each step. Samples were isolated from these control sets and characterized using FTIR for comparison. TA/DGEBA composite samples were prepared by isolating shavings from the epoxy bars described previously. Samples were scanned 4 times and normalized to the phenyl peak at 1605 cm^{-1} using Spectra (PerkinElmer, Seer Green, Beaconsfield, UK). Absorbance values were calculated using Spectra (PerkinElmer, Seer Green, Beaconsfield, UK) and were averaged between samples.

Optical Microscopy was performed using a Zeiss optical microscope (Zeiss, Thornwood, NY, USA). Samples were prepared by pouring 5 mL of sample cured at 150 °C for 45 minutes onto a microscope slide. Spacers were used on either side of the sample to ensure consistent sample thickness and a microscope slide was placed on top. Image analysis was done using ImageJ (National Institute of Health, Bethesda, MD, USA).

Dynamic Mechanical Analysis (DMA) was performed on all samples using Q800 Dynamic Mechanical Analyzer (TA Instruments, Newcastle, DE, USA). Samples were prepared of dimensions 5.5 cm x 1.2 cm x 0.35 cm by pouring prepared solutions into silicone molds and then cured. Samples were polished to remove remaining silicone from their surfaces. A dual cantilever mechanical test was performed at a frequency of 1 Hz and displacement of 0.15 µm. Temperature was increased at a rate of 15 °C per minute from 30 °C to 250 °C. Initial E’ was calculated by averaging the E’ values for samples at 45 °C. Three samples were run at each TA concentration and were averaged. T_g values were calculated by measuring the temperature of the peak of the tan(δ) curve using Universal Analysis (TA Instruments, Newcastle, DE, USA).

Differential Scanning Calorimetry (DSC) was performed on shavings of the epoxy samples using a Q2000 Differential Scanning Calorimeter (TA Instruments, Newcastle, DE, USA). Samples of 12±1.2 mg were loaded into aluminum pans and run using a heat/cool/heat cycle from –75 °C to 200°C with a heating and cooling rate of 25 °C/min. Three samples were run at each concentration and the mean glass transition value of the second heat curve was calculated as the midpoint of the incline observed on thermograms and averaged for each concentration using Universal Analysis (TA Instruments, Newcastle, DE, USA).

Mechanical testing was performed using a compression fixture on a Mechanical testing frame (MTS Instruments, Eden Prairie, MN, USA). Cylindrical samples were prepared with dimensions of 24.7 being and respectively. Samples were loaded to break, which was determined by observable cracking and fracture on the surface of the part. Toughness values were obtained by integrating the stress/strain curves using OriginPro 2017 (OriginLab Inc., Northampton, MA, USA).

Hardness testing was performed on epoxy samples using a digital Shore D Hardness Durometer (YescomUSA, La Puente, CA, USA). Cylindrical samples were prepared with diameter 24.7±0.1 mm and length 14.6±0.5 mm. Samples were placed on a stable surface. The indenter was rested 20mm away from the surface of the material using a ring stand and a clamp. The durometer was lowered manually until it contacted the surface of the epoxy material. The durometer was manually pressed down and the maximum hardness value was recorded. This procedure was repeated 15 times per sample.

Statistical analysis was performed using JMP (SAS Institute, Cary, NC, USA). A student's t-test was run to compare samples. A p-value <0.05 was used to indicate statistically significant differences between samples. Regression analysis was performed using OriginPro 2017 (OriginLab Inc., Northampton, MA, USA). Results were fit to an exponential decay and linear models, and the reported equations and standard error (S_e) values were output by the software after regression analysis. S_e values <0.05 were determined as appropriate fits for the regression.

3.4 Results And Discussion

3.4.1 Understanding Initial Behavior of System:

TA and DGEBA samples showed an observable color change when mixed at 150 °C in nitrogen atmosphere over a 40-minute period (Figure 3). Initially, at room temperature and upon heating, the samples were a light tan, opaque mixture in which visible clumping of TA was observed. After 20 minutes at elevated temperature the solution was found to turn a darker brown color with a significant increase in translucency with small clumps of TA powder stirring with the solution. After 45 minutes, these aggregates disappeared altogether, and the solution was significantly more viscous and darker. At 60 minutes the samples were completely solid. Optical microscopy of these samples further indicated that at the micro-scale clumps and aggregates of TA in DGEBA solution decreased in size as the solution was mixed at elevated temperature (Figure 3.3). Further, after heating to 175°, samples showed a darkening in color because of increased TA loading to the point where extremely highly loaded samples became very dark brown in color (Figure 3.4). Optical microscopy revealed leftover bubbles from mixing, but not observable clumping at this scale. The solution color changed from a very light, translucent tan to a significantly more browned but still translucent sample as TA loading increased. Samples further reacted at 175 °C were darker in color than samples of the same composition that were at 150 °C for 50 minutes.

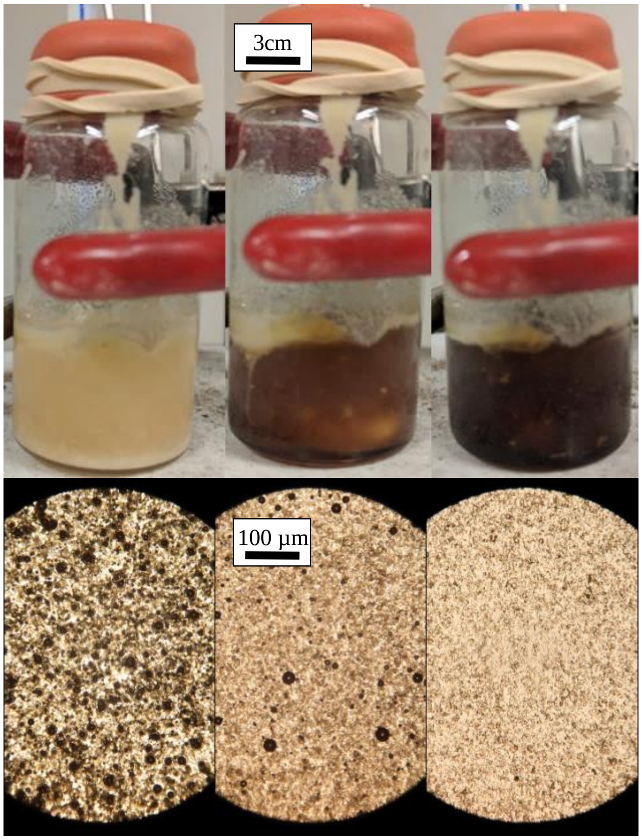

Figure 3.3: Top - Photographs of the 28.6% TA/DGEBA solution heated at 150°C for 0, 20, and 40 minutes (left to right). Bottom - optical microscopy of the DGEBA solutions at 0, 20, and 40 minutes (left to right).

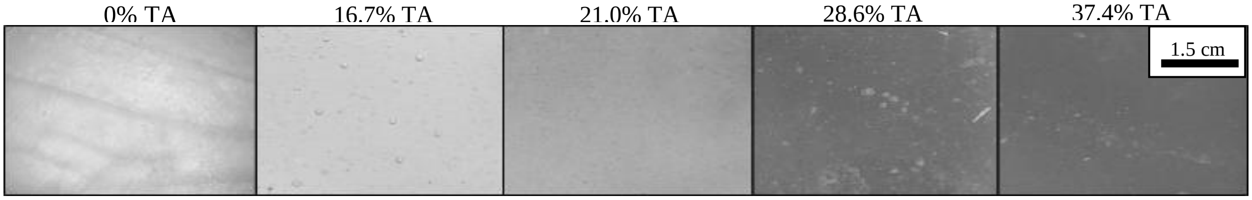

Figure 3.4: Optical Microscopy for TA/DGEBA mixtures after curing. Samples (from left to right) are 0% TA, 16.7% TA, 21.0% TA, 28.6% TA, and 37.4% TA.

To understand why visible changes in compatibility were observed for these composite systems, fourier transform infrared (FTIR) spectroscopy was performed on 28.6% TA samples at 0 minutes, 20 minutes, and 40 minutes as well as after the 4 hour cure at elevated temperature. The relative absorbance value of the epoxy ring (915 cm^{-1}) was found to decrease as the compatibility of the overall system increased (Figure 3.5). The oxirane absorbance was found to decrease as an exponential decay ($S_e<0.05$) as the two chemicals were mixed for increasing amounts of time, which may indicate 1st order reaction kinetics. FTIR output for all samples cured at 175 °C lacked the epoxy peak visible in the DGEBA FTIR results were normalized to the initial epoxy ring absorbance for the composite system at room temperature but after thorough mixing.

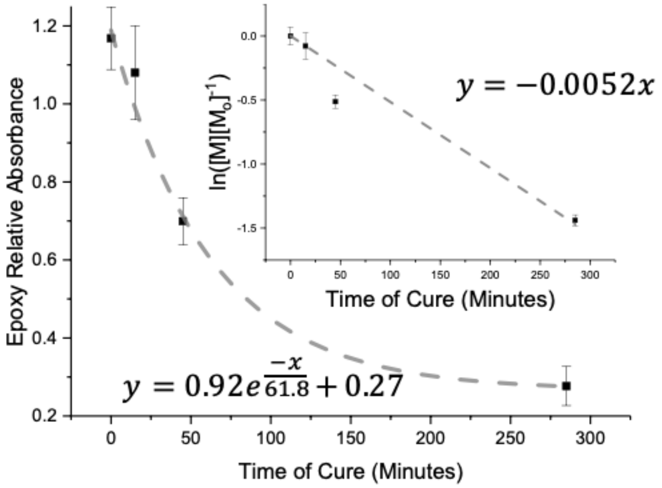

Figure 3.5: FTIR Analysis for the relative epoxy peak absorbance as a function of reaction time. Results were fit to an exponential decay with respect to the original epoxy peak absorbance.

Table 3.2: Thermomechanical and thermal stability results for the TA/DGEBA composites. Samples denoted with "*" are significantly changed compared to the control sample ($p<0.05$).

Sample	Wt. % TA	E' (GPa)	T_d (ºC)	$\nu_c \times 10^5$ (mol/m^3)	ϕ_c	T_g (ºC)	
						DMA	DSC
Control	0	1.90 ± 0.01	-----	2.36 ± 0.01	-----	96.4 ± 1	90.3 ± 6
0.5	16.7	1.95 ± .08	308±36 and 432±11	2.45 ± 0.10	0.09±0.00	143 ± 11*	112 ± 17*
0.66	21	2.38 ± .06*	424±23*	3.00 ± 0.08*	0.21±0.02*	186 ± 6*	158 ± 13*
1	28.6	3.03 ± 0.1*	419±23*	3.82 ± 0.13*	0.19±0.03*	199 ± 3*	165 ± 9*
1.5	37.4	3.14 ± 0.06*	428±23*	3.96 ± 0.08*	0.20±0.01*	201 ± 4*	167 ± 10*

To help probe the behavior of this system TGA was performed (Figure 3.6). T_d and residual char fraction (ϕ_c) were obtained from the output (Table 3.2). Output thermograms showed the T_d of the DGEBA/TA composites had significantly increased compared to TA and the bulk of DGEBA degradation. TA degradation in nitrogen began at 180 °C and the temperature of peak mass loss occurred at 248 °C which was found to be consistent with what was found in literature.[81] TA continued to thermally degrade until 325 °C at which point a more stable char was formed and the rate of mass loss was significantly decreased which was consistent with literature.[81] TGA results indicated that DGEBA resin does not thermally degrade at the reaction temperatures (150 and 175°C). The bulk of the DGEBA sample mass loss began at 250 °C. The temperature of peak mass loss was 375 °C. A second T_d was observed at higher temperature for the DGEBA resin. All EPON/TA composites had significantly increased thermal stability as compared to the control samples, but the higher T_d of the EPON resin was not found to be significantly different than the EPON/TA composites. Φ_c increased with TA loading from the 0% to 16.7% and then finally the 28.6% sample (0.007, 0.09, and 0.21 respectively). However, increases in residual char were not observed past this point with additional TA-loading as both the 28.6% and 37.4% samples had a residual char fraction of 0.19 and 0.2 respectively. In all cases, the amount of residual char was found to be significantly increased as compared to the control DGEBA samples ($p<0.01$), however they were significantly decreased as compared to the TA control samples which has a residual char fraction of 0.3. Previous researchers have indicated that the galloyl components of TA are critical to its ability to char. The fact that TA/DGEBA composite systems are unable to char as much as the TA control sample is indicative of a decrease in the presence of galloyl groups. This is because previous researchers have shown that the galloyl groups on TA are important to its ability to char.[81]

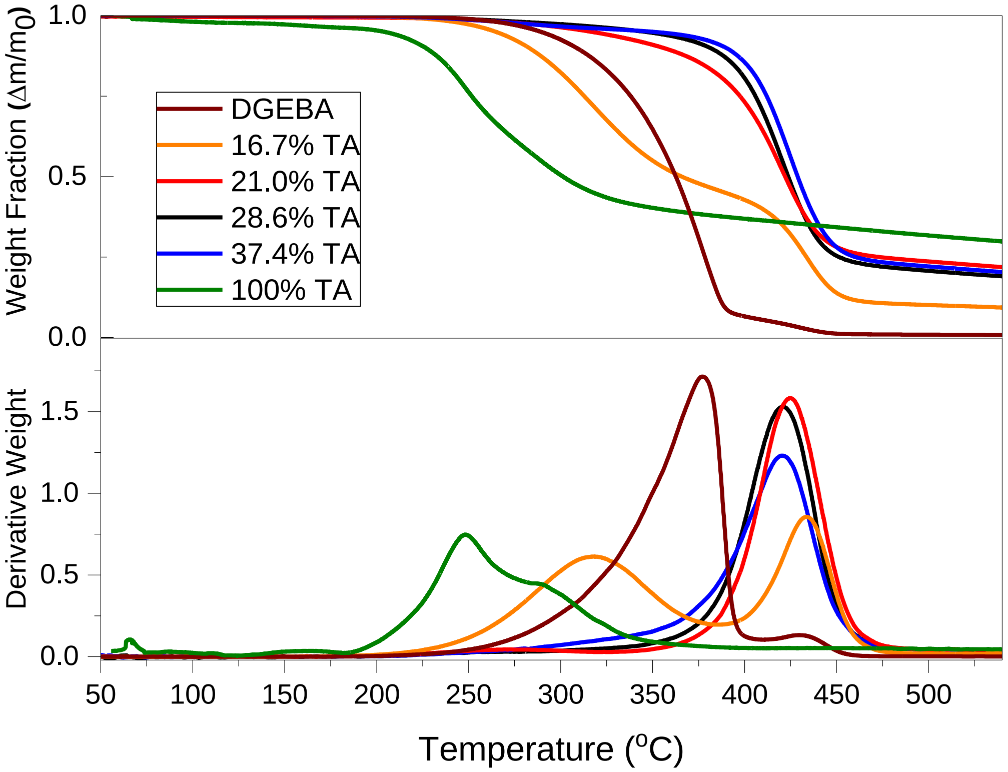

Figure 3.6: Thermograms for DGEBA/TA composites as well as DGEBA and TA control samples.

To understand the mechanism of thermal degradation, FTIR was performed on two DGEBA samples (supplemental information). The result from this test showed a significant decrease in the C-O-C oxirane stretch absorbance peak at 915 cm^{-1} and a significant increase in the -OH peak at 3507 cm^{-1} in the sample that was heated at 400 °C as compared to the sample at room temperature. This indicated that thermal degradation of DGEBA below 400 °C was correlated to the degradation of the epoxy ring on the molecule.

The change in compatibility and the color change observed through optical microscopy of these samples indicates that TA is becoming more soluble in the DGEBA matrix as the temperature of the solution is increased and the sample is allowed to sit for long periods of time. As the samples become more visibly brown and transparent, FTIR results indicate that at temperatures below the point of thermal degradation of epoxy rings in nitrogen, the absorbance of the epoxy ring in the solution decreases. In this way, the addition of TA into the DGEBA resin is directly responsible for the change in epoxy ring absorbance. Further, as TA is loaded into DGEBA, the thermal stability and residual char fraction of the composite materials is significantly increased as compared to the DGEBA control sample; however, while the residual char fraction was increased in all TA/DGEBA composite samples compared to the DGEBA sample, it was decreased compared to the TA control.

The preliminary explanation for these behaviors is that TA and DGEBA were reacting through a ring-opening polymerization reaction between the gallol hydroxyls of TA and the epoxide ring of the DGEBA molecule (Scheme 1). The chemical reaction of phenol and an epoxy ring has been seen in previous literature at temperatures below 150 °C (at 100 °C);[82] thus, it is believed that the observed compatibility increase was due to TA being surface functionalized with DGEBA through a ring-opening reaction. At the macro scale, the result of this reaction between these two molecules is a thermoset polymer (Figure 3.7). Optical microscopy, FTIR analysis, and thermal stability support this claim. As the reaction proceeds, the compatibility of the system increases as more TA molecules are modified (hydrophobized) by either DGEBA molecules or by epoxidized-TA molecules. However, at elevated temperature this reaction is limited by the initial limited solubility of the TA molecules. Once mixed, TA and DGEBA can only react at the interface between the TA and DGEBA phases which is at the surface of the TA agglomerations. The molecules on the interior are protected by the surrounding TA molecules. As TA molecules on the surface become more compatible in the DGEBA matrix, they dissolve into the DGEBA and undergo further reaction. This also exposes fresh, unreacted TA molecules from within the agglomerates.

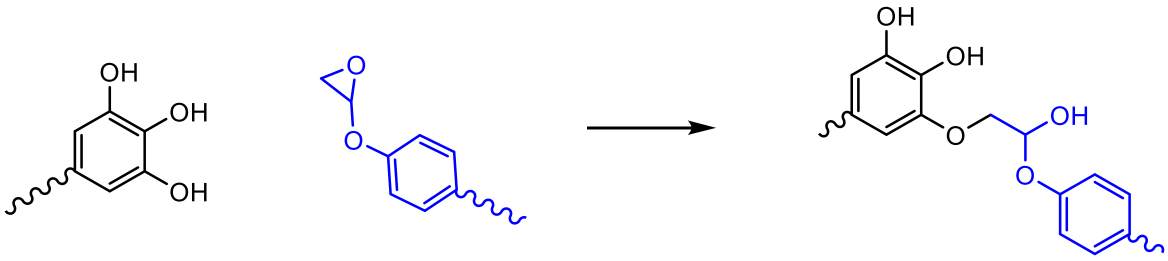

Figure 3.7 Reaction scheme for a phenolic group and epoxy.

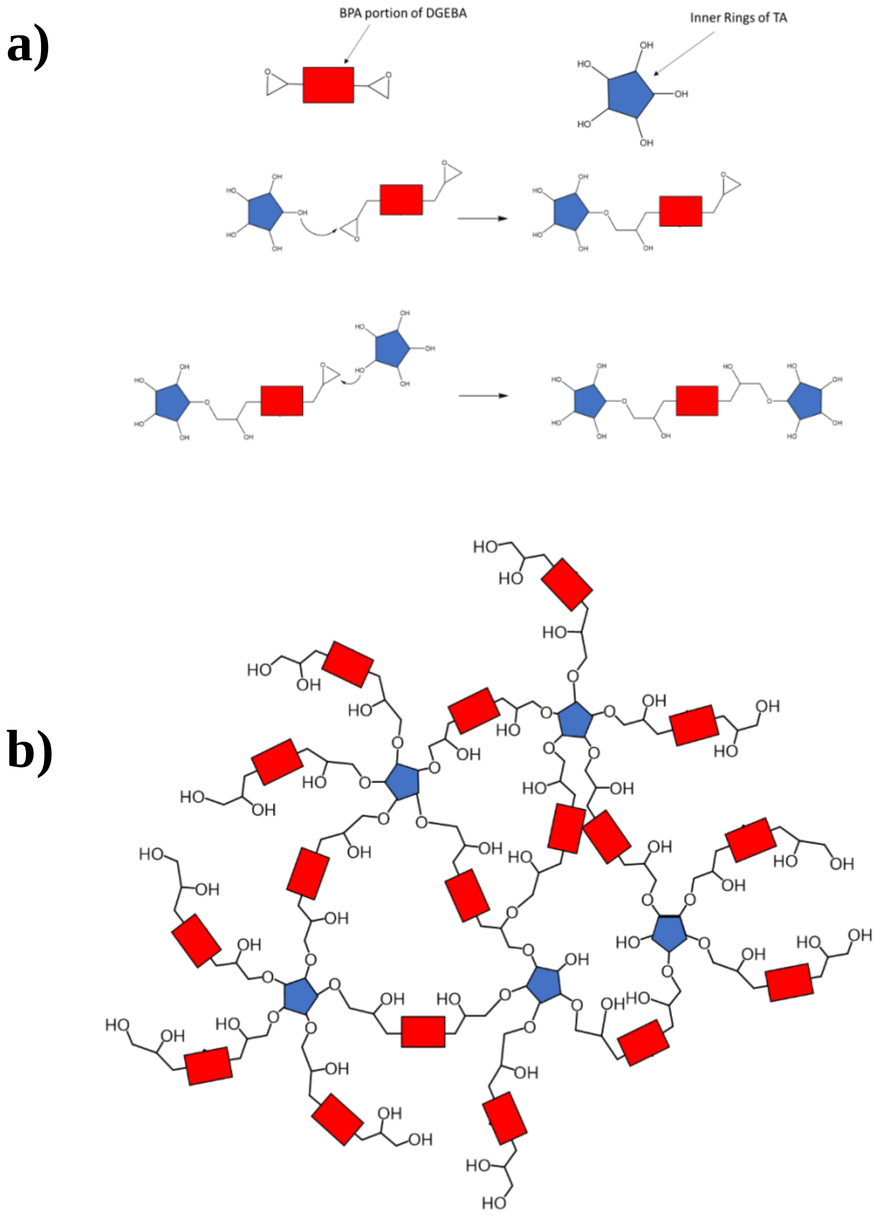

Figure 3.8: a) A visualization of the initial stages of the reaction pathway. TA is surface functionalized with DGEBA and is then able to react with additional TA molecules. b) A macro-scale visualization of the resulting thermoset network polymer in which a dense, molecular network is achieved.

The resulting materials cured at 175 °C for 4 hours have increased thermal stability as compared to the comparative novolac samples, which is indicative of a chemical bonding change within the samples. The epoxy groups on DGEBA (Figure 3.9) and the phenol groups on TA[81] thermally degrade below 400 °C, and. In the 16.7% sample, the one containing an excess of epoxy groups, the resulting thermogram shows indications of residual unreacted phenol and epoxy groups with the thermal degradation at 308 °C but also shows clear evidence of phenol-epoxy reaction with the second degradation at 432 °C. The observed degradation at 308°C is indicative of unreacted galloyl groups on TA that are constrained within the networking system, but that are more readily available for degradation than the surrounding network. As such, they degrade at a temperature above the unreacted galloyl group on TA, but at a temperature below the reacted network system surrounding them. The 21.0% sample shows only 1 peak of thermal degradation at 424 °C, however thermal degradation is clearly initiated at a temperature comparable to that of the peak associated with degradation of unreacted phenol and epoxy groups. In each of these samples, the excess of epoxy groups added to the sample are not fully reacted as evidenced by the thermograms. The 28.6% and 37.4% samples show one sharper peak (419 °C and 428 °C respectively) indicating that the reaction has fully completed at this point, however the early onset of thermal degradation is indicative of residual unreacted epoxy and phenol groups. There is little benefit to thermal stability by adding additional TA past the 28.6% sample at which an equal molar ratio of epoxy and phenol are added. This result further indicates that while a reaction is occurring between the phenol and epoxy groups, there is some limitation to the crosslinking ability of the thermosetting polymer system and that adding additional TA to the solution does not change its ability significantly.

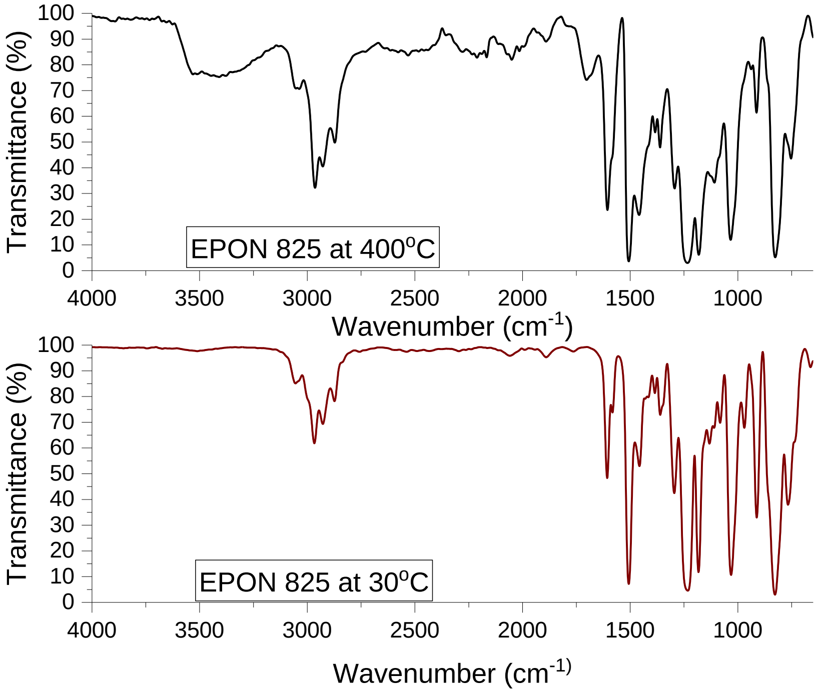

Figure 3.9: Output FTIR results for DGEBA at room temperature and at 400°C. Normalized results for the change in the epoxy peak (915 cm$_{-1}$) and the hydroxyl peak (3507 cm$_{-1}$) from FTIR. Results indicate that the epoxy absorbance significantly decreased ($p<0.05$) and the phenol absorbance significantly increased ($p<0.05$). This result suggests that the epoxy ring degrades.

The increased thermal stability of DGEBA/TA samples is expected with ring opening polymerization. The fact that thermal stability does not correlate with TA loading level indicates TA is not capable of fully crosslinking the epoxy polymer even at elevated temperature. Initial significant increases in thermal stability and char formation indicate that TA is crosslinking into the epoxy system. However, as TA is added such that an equal molar amount or an excess of gallol hydroxyls are present, TA is capable of crosslinking the polymer to some maximum amount at which point further crosslinking is not possible. This is likely due to TA being sterically limited in its crosslinking ability. Even though TA has 25 potential reactive sites based on its gallic functionality, they do not all have the same reactivity, and their reactivity changes throughout the reaction. Three of these phenolic sites are covalently attached to the phenyl ring at the end of each arm of the TA molecule, each site meta to the next, meaning that 15 gallol hydroxyls are at the edge of the molecule but in five densely-packed groups of three. Once a single one of these three sites has crosslinked into the DGEBA system, it becomes more difficult to crosslink the other two hydroxyls at the end of that arm due to the proximity of the gallic hydroxyls on this ring. Once a second group has reacted it becomes even more difficult to crosslink the last site due to the sheer density of the gallic groups at the end of the di(gallic acid) arms. Further, there are 2 additional gallol hydroxyls attached to the inner phenyl ring of each di(gallic acid) arm meaning that 10 of the 25 gallol hydroxyls are contained within the larger TA molecule. These sites are significantly more difficult for DGEBA molecules to reach than the outside gallol hydroxyls because they are contained within the molecule itself. As the reaction proceeds, the outer gallol hydroxyls become more modified and the TA molecule becomes more compatible with the system. The inner gallol hydroxyls should interact with additional DGEBA molecules, however once one of the two gallol hydroxyls has reacted the second becomes significantly less reactive due to steric limitations. The overall reactivity of is thus dependent on the positioning and availability of the gallol hydroxyls and oxirane groups, and as the reaction continues the availability of both the 15 gallol hydroxyls on the surface of the molecule and the 10 contained within the molecule changes, but generally decreases. Because the TA molecule is much larger than the DGEBA molecule and cannot crosslink into the network fully due to steric limitations in this way, it is reasonable that the resulting polymer has a crosslinking limit.

3.4.2 Thermomechanical Characterization

To further probe the crosslinking ability and properties of the materials, TA-crosslinked epoxy samples as well as comparative novolac epoxy samples were studied via DMA and DSC (Figure 3.10 and Figure 3.11). E’ at room temperature and T_g were measured (Table 3.2). Epoxy samples cured with commercially available triethylene tetramine (TETA) were found in the literature to have E’ and T_g near 2 GPa and 135 °C respectively.[83] Other researchers determined these values for other bio-sourced polyphenolic-hardened epoxy networks and found E’ and T_g values near 1 GPa and 150 °C and respectively.[84] DMA of TA hardened epoxy showed E’ and T_g initially increased significantly from the 16.7% sample (1.95 GPa and 143 °C) to the 21.0% sample (2.38 GPa and 186 °C) as well as from this sample to the 28.6% sample (3.02 GPa and 199°C). However, past this point the T_g and E’ increased monotonically with increasing TA concentration for the 37.4% sample (3.14 GPa and 201°C). The E’ and T_g (1.90 GPa and 96.4°C of the comparative novolac sample were found to be significantly decreased as compared to all of the

TA-loaded samples. The T_g measured by DSC (Sample 0.5: 112°C, Sample 0.66: 158°C, Sample 1: 165°C, Sample 1.5: 167°C, and Control (comparative novolac): 90.3°C) was lower at each TA content than those measured by DMA, but the trends observed were consistent between characterization techniques. As TA loading was increased, the resulting T_g both from DMA and DSC was more distinct, but the most distinct sample was the comparative novolac sample. The TA-hardened epoxy samples were also found to have a significantly increased E' and T_g as compared to aliphatic amine-hardened samples measured by previous researchers[83]

The concentration of network chains, or the crosslink-density, (ν_c) is the number of moles of network chains per unit volume of a cured polymer.[85] Crosslink density of highly crosslinked thermosets can be determined by by using the equation of state for rubber elasticity[85] which is,

$$\nu_c = \frac{E'}{3RT} \qquad (1)$$

Where, E' is the tensile storage modulus in the rubbery plateau, T is the temperature in Kelvin corresponding to the storage modulus value and R is the gas constant. The correlating crosslink density for these TA-hardened epoxy samples was calculated (Table 3.2). It was found to increase significantly as TA was loaded into the polymer sample (2.45 x 10_5 mol/m$_3$ for the 16.7% samples and 3.0 x 10_5 mol/m$_3$ for the 21.0% samples). However, as TA loading increased the crosslink density between the 28.6% sample and the 37.4% sample (3.82 and 3.96 mol/m$_3$ respectively) did not significantly increase. This provided further verification that there is a crosslinking limit within this thermosetting system that occurs at a TA loading at which a 1:1 molar ratio of DGEBA epoxy to TA gallol-hydroxyl. The crosslink density for the comparative novolac samples was calculated (2.63 mol/m$_3$) and found to be significant decreased as compared to the 0.66, 1.0, and 1.5 samples. This was expected due to the difference in phenol equivalent weights between TA and the novolac resin. When comparing the relative crosslink density of the TA-hardened epoxy to commercially available aliphatic amine samples (3 x 10_5mol/m$_3$)[83]and other bio-based phenolic hardener samples (1 x 10_5 mol/m$_3$),[84] in highly loaded TA samples the crosslink density is significantly increased. This is likely due to the increased availability for crosslinks in TA (25 sites/molecule) as compared to amine hardeners – such as TETA (6 sites/molecule), and other polyphenolic systems (3-6 sites/molecule).[84]

The elevated T_g of TA-hardened epoxy samples observed in both DSC and DMA as compared to amine-hardened or other polyphenolic hardeners is also likely due to increased crosslinking site density in TA. Even if only seven of the gallol hydroxyls (28%) react on average per molecule the resulting polymer should have a higher crosslink density than TETA (6 sites/molecule) and polyphenolic hardeners (3-6 sites per molecule). The trends observed for crosslink-density and glass transition are the same, which is further indication that the two properties are related. The fact that these properties do not exactly correlate with TA loading level further indicates TA is not capable of fully crosslinking the epoxy polymer even at elevated temperature, which is consistent with results found from TGA and crosslink density. TA loading is again found to crosslink the polymer to some maximum amount at which point further crosslinking is not possible due to steric limitations.

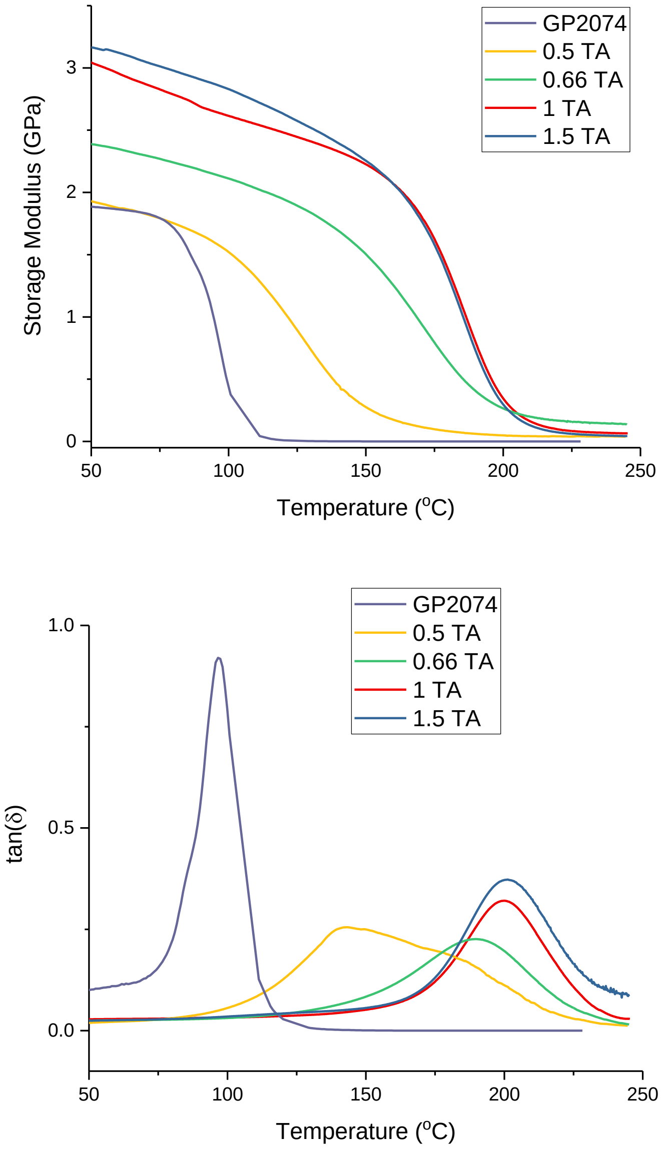

Figure 3.10: DMA results for the 4 TA-hardened epoxy samples including bending storage modulus (top) and tan(δ) (bottom).

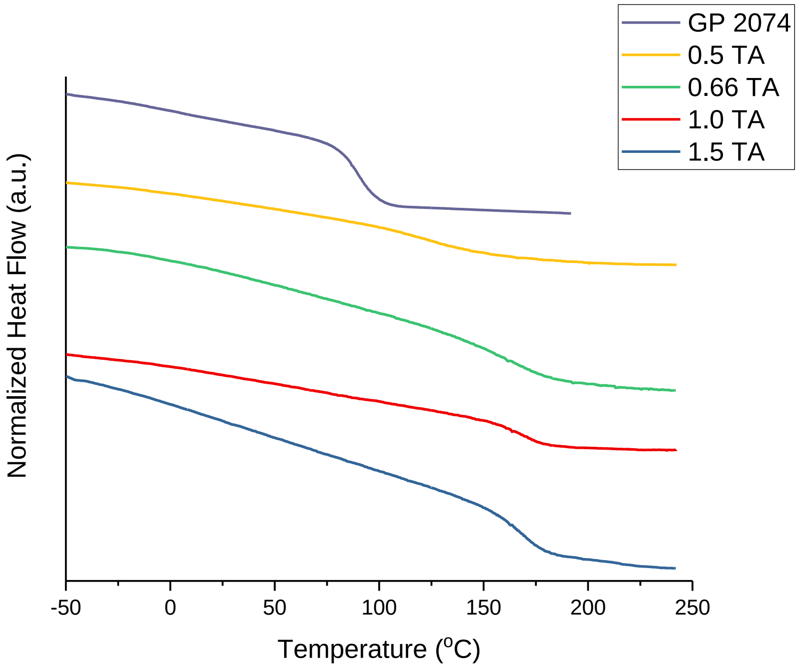

Figure 3.11: DSC heating results for the 4 TA-hardened epoxy samples.

The resulting T_g measured by DSC and DMA of both the 28.6 and 37.4%wt TA-hardened epoxy samples was found to be comparable if not higher than currently commercially available high T_g epoxy materials found in circuit boards[86-88] and other polyphenolic hardeners found in the literature (127-154°C). It was also found to be higher than and comparable to commercially available high T_g epoxies used in other applications such as high temperature laminates, coatings, and advanced composites such as 4-4'-diaminodiphenylsulfone (DDS or DAPS) (T_g 177°C) and others (T_g 160-180°C).[48,49,89,90] However, at lower loading levels TA-hardened thermosets showed thermomechanical properties similar to aliphatic amine-hardened epoxy polymers and other polyphenolic hardeners. The loading level of TA in DGEBA changed resulting thermomechanical properties, allowing the properties of the material to be tuned to the desired application.

3.4.3 Mechanical Testing

Mechanical testing results indicated that with increased TA loading into the polymer, a significant change in the compressive behavior was observed (Figure 3.12). Increased TA loading significantly increased the compressive modulus of the resulting thermoset (Figure 3.13 and Table 3.3). In all samples, an elastic deformation zone was observed after an initial delay at low strains.

However, in samples 0.5, 0.66, and 1.0, a plastic deformation zone was observed after the initial elastic deformation. The length of the plastic deformation-zone was found to decrease with increasing TA loading, which was indicative of more networked systems as TA loading increased. These results indicate that TA is crosslinking into the system but is not fully crosslinking at low loading levels. Domains of crosslinked TA and DGEBA exist and are more weakly bound to each other than the networks within. When the samples are compressed with significant stress, these loosely-bound domains are capable of sliding past each other, most likely due to bond breaking between domains, and allow for compression to take place. This indicates that while global crosslinking density may be increasing, locally there are changes in crosslinking density that allow for plastic deformation to take place. However, in the novolac and 1.5 sample this behavior is not observed. The reasoning for this behavior is that the samples are more efficiently networked, even between domains, and are therefore more capable of resisting the compressive force.

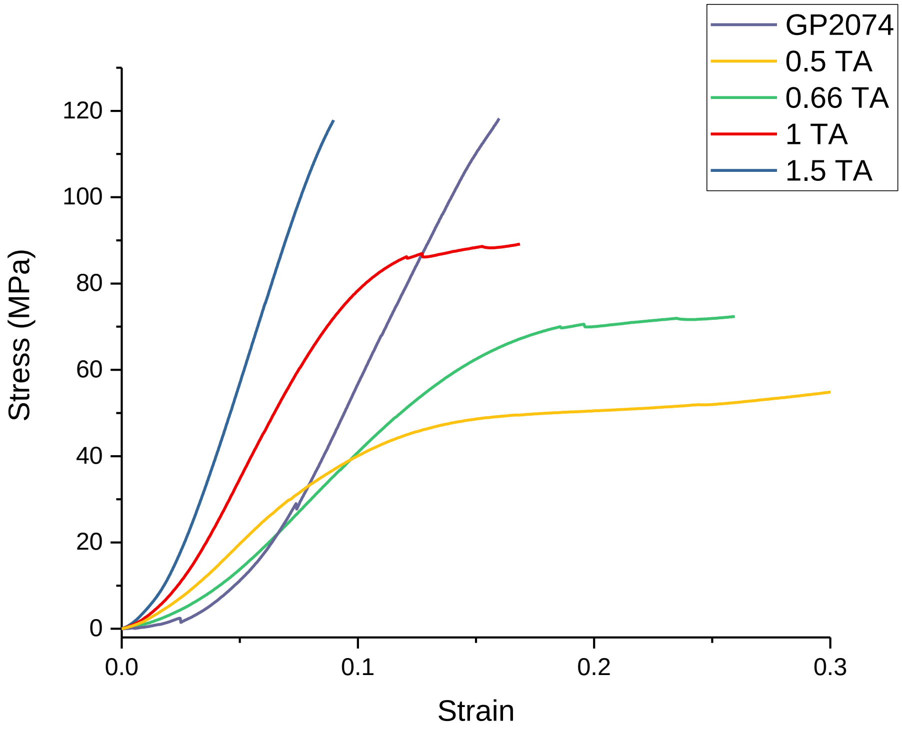

Figure 3.12: The measured stress/strain curve for the samples compared for the compression test.

Table 3.3: Mechanical testing results for the control set and the TA/DGEBA composites. Samples denoted with "*" are significantly changed compared to the control sample ($p<0.05$).

Sample	Wt. % TA	Compressive Modulus (GPa)	Fracture Stress (MPa)	Toughness (MJ/m$_3$)	Shore D Hardness
Control	0	1.21 ± 0.08*	120 ± 11	7.05 ± 0.75	78 ± 4.7
0.5	16.7	0.53 ± 0.15*	51 ± 20*	9.65 ± 0.18*	70 ± 5.8*
0.66	21	0.56 ± 0.04	72 ± 15*	11.89 ± 0.80*	80 ± 3.9
1	28.6	1.07 ± 0.16	89 ± 15*	9.51 ± 0.49*	88 ± 1.9*
1.5	37.4	1.74 ± 0.10*	120 ± 8	4.64 ± 0.41*	91 ± 1.1*

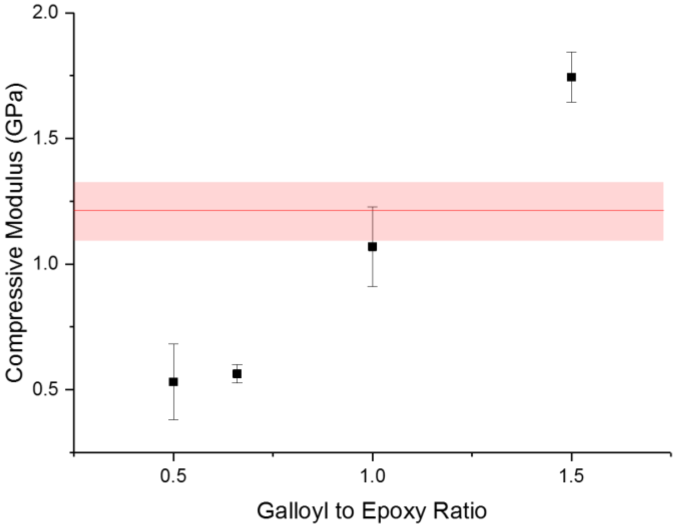

Figure 3.13: Compressive modulus results for both the comparative novolac sample (indicated in red) and the TA/DGEBA composites.

As was shown in the previous section, there exists a crosslinking limit within the system. The proximity of the reactive, phenolic groups on TA limits the crosslinking ability of the molecule. However, as TA is loaded into the samples at a 1:1 molar ratio and in excess, the resulting polymers exhibit increased modulus and fracture stress, even between themselves, which do not have significantly different crosslinking densities (Table 3). The reasoning for this behavior is believed to be that while the crosslinking limit is not changing, more TA is in the system per volume in the

1.5 sample than the 1 sample. This means that TA is crosslinking less per molecule on average in the 1.5 sample than the 1 sample, but there is more TA in the network in the 1.5 sample than the 1 sample. Because TA is the stiffer molecule, it is expected that the stiffness of the overall system would increase sequentially. The T_g of the polymer does not follow this same trend with increased TA loading. It is believed to be more sensitive to the crosslinking density than the concentration of TA.

In every sample other than 1.5, the sample did not fail all at once but rather small pieces of thermoset snapped off and shot away from the tester, often near the surface of the polymer. This cracking, rather than total failure, is due to the inconsistent crosslink density across the system. Less-crosslinked sections of the thermoset are the first to fail, cracks are formed and grow along the least-densely-crosslinked sections of the polymer, and then once the crack reaches a certain length the densely networked section breaks off.

The variability in crosslink density is consistent with results found in optical microscopy, where small aggregates are observed at the macro scale. This conclusion is also consistent with the DSC curve and the tan(δ) obtained via DMA in which significantly broader Tg peaks were observed in the lightly TA-loaded samples (0.5, 0.66, and 1.0) than in the novolac sample or the 1.5 sample. This broad glass transition for the bulk material is indicative of a range of local network densities that have different, local T_g values.

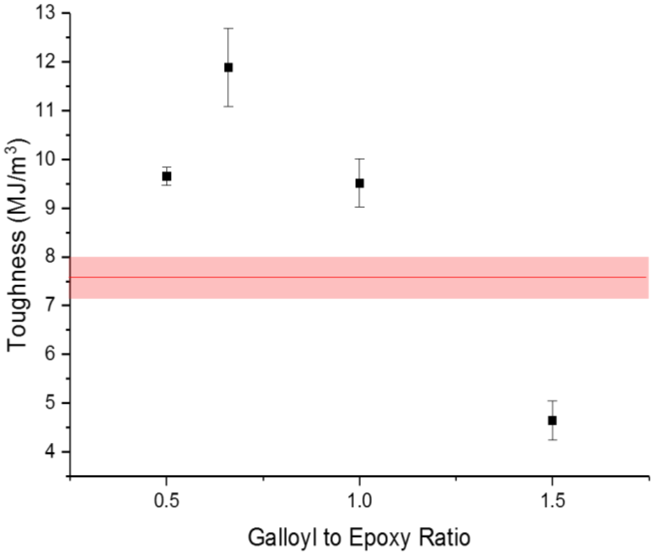

Figure 3.14: Toughness values for the comparative novolac sample (labeled in red) and the TA/DGEBA composites.

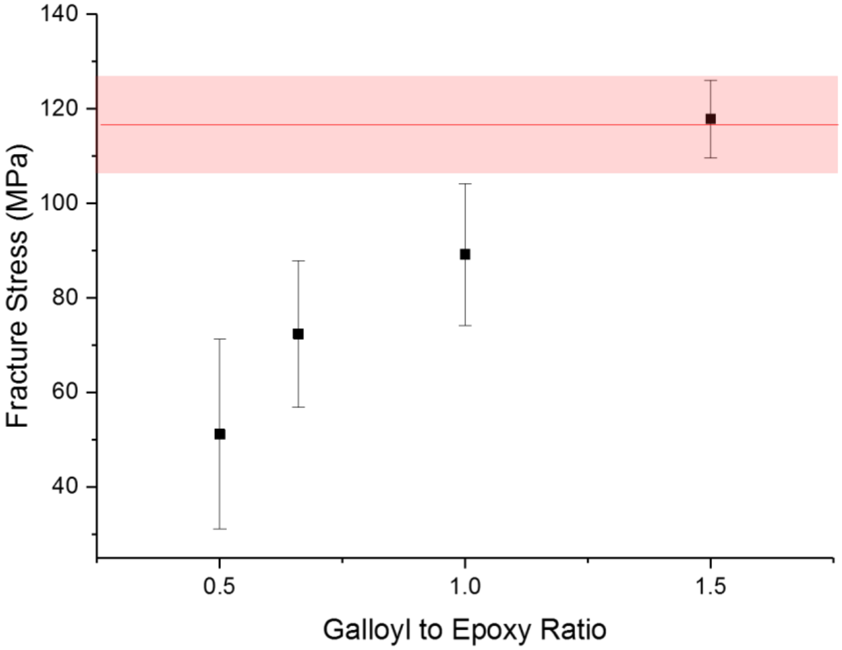

Figure 3.15: The measured fracture stress from mechanical testing, with the comparative novolac indicated in red.

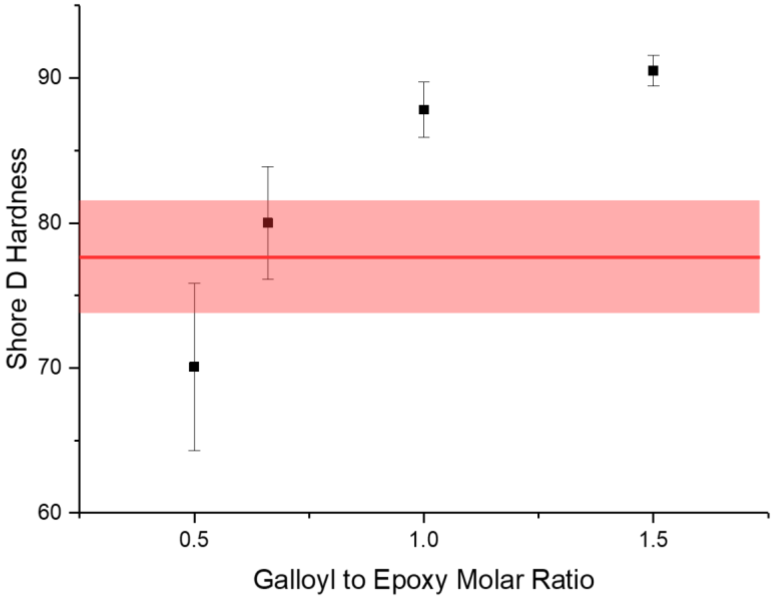

Figure 3.16: Hardness values for the comparative novolac (in red) and the TA/DGEBA composites.

The 0.5, 0.66, 1, and 1.5 samples had resulting compressive moduli of 0.53, 0.56, 1.07, and 1.74 GPa respectively, with the 0.5 and 0.66 samples having moduli significantly less than the novolac sample and the 1.5 sample having a modulus significant higher than the novolac sample (Figure 3.13). Toughness values were also significantly dependent upon TA-concentration in the samples (Figure 3.14). Samples 0.5, 0.66, 1, and 1.5 were found to have toughness values of 9.65, 11.89, 9.51, and 4.64 MJ/m$_3$ respectively and the novolac sample had a toughness value of 7.05 MJ/m$_3$ (Table 3.3). As can be seen, plastic deformation in the 0.5, 0.66, and 1.0 samples added to the overall toughness of the polymer, although their overall resistance to compression was less than that of the novolac or the 1.5 sample. Fracture stress was also dependent upon the amount of TA loading, as the 0.5, 0.6, 1, and 1.5 samples were found to have fracture stresses of 51, 72, 89, and 120 MPa respectively while the novolac sample had a fracture stress of 120 MPa (Figure 3.15). Finally, hardness values were largely dependent upon the TA loading with an indication that on the surface of the material, the 1 and 1.5 samples are capable of crosslinking effectively, but the 0.5 and 0.66 samples are unable to fully crosslink (Figure 3.16). Shore D hardness values were determined to be 70, 80, 88, and 99 for the 0.5, 0.66, 1, and 1.5 samples respectively while for the novolac the hardness was 91. These results indicate that the addition of TA increases the stiffness of the polymer in compression, which corroborates the results from previous testing. The results also indicate that highly loaded TA samples are significantly stiffer in compression than the novolac sample. Further, as TA is loaded into the thermoset, the surface of the polymer becomes harder.

3.5 Conclusions

Currently available epoxy hardening agents have unintended health and environmental impacts. There is a need for an alternative, more sustainable alternative epoxy hardener to be developed that is capable for use industrially, especially in high-temperature applications. TA is a polyphenolic molecule found in trees that has been found to crosslink epoxy containing compounds at elevated temperature. Further, TA is available in high quantities industrially as it is used for tanning leather. Because of its high concentration of crosslinking sites, TA was found to be able to react with DGEBA resin to form a densely crosslinked epoxy polymer with resulting high thermal stability and thermomechanical properties, something seen before for TA in previous literature but never at this scale. The resulting thermomechanical properties and T_gs were significantly higher than those previously reported for TETA hardened epoxy, and within the range of several commercially available high T_g epoxy thermosets, such as dicyandiamide and 4,4'-diaminodiphenyl sulfone. The resulting mechanical properties and T_g could be tuned by changing the loading level of TA in the DGEBA resin. The resulting thermosetting materials show promise in a variety of applications. Because the synthesis is simple, it is expected that this process can be easily scaled-up to larger industrial processes in which TA can potentially replace novolac resins in ongoing processes. With an industrially available, comparably priced, more sustainable, and effective epoxy hardening agent available to the market, it is the hope of the authors that this material can be utilized to lessen the health and environmental impacts of epoxy material synthesis.

3.6 Future Work

Current limitations in this work are that the reaction must proceed at high temperature in order for acceptable compatibility and mechanical properties to be observed. Future work will involve determining appropriate methods to encourage the crosslinking reaction to proceed at lower temperature.

3.7 Acknowledgements

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3.8 References

1. Kuruppalil, Z. In *Green Plastics: An Emerging Alternative for Petroleum Based Plastics?*, IAJC-ASEE International Conference, Hartford, Connecticut, Hartford, Connecticut, 2011.

2. Kuruppalil, Z. In *Plastics packaging: the challenge of going green*, The First International Conference on Green and Sustainable Technology, University of North Carolina A&T, University of North Carolina A&T, 2011.

3. Mwanza, B. M.; Mbohwa, C., Drivers to sustainable plastic solid waste recycling: a review. *Procedia Manufacturing* **2017,** *8*, 649-656.

4. Peng, L.; Deng, Y.; Yi, P.; Lai, X., Micro hot embossing of thermoplastic polymers: a review. *Journal of Micromechanics and Microengineering* **2014,** *24*, 1-23.

5. Chen, Z.; Yang, F.; Meguid, S., Multi-level modeling of woven glass/epoxy composite for multilayer printed circuit board applications. *International Journal of Solids and Structures* **2014,** *51* (21-22), 3679-3688.

6. Haugan, E.; Per Dalsjo, P., Characterization of the material properties of two FR4 printed circuit board laminates. FFI Rapport, 2014.

7. Composite Adhesives Market by Resin (Epoxy, Polyurethane), Component (One-Component, Two-Component), Application (Automotive & Transportation, Marine, Aerospace, Wind Energy), and Region - Global Forecast to 2022. (accessed October 4).

8. Wang, H.-h.; Zhou, X.-r.; Liu, Q.; Chen, G.-Q., Biosynthesis of polyhydroxyalkanoate homopolymers by Pseudomonas putida. *Applied Microbiology and Biotechnology* **2011,** *89* (5), 1497-1507.

9. Liu, Q.; Luo, G.; Zhou, X. R.; Chen, G.-Q., Biosynthesis of poly(3-hydroxydecanoate) and 3-hydroxydodecanoate dominating polyhydroxyalkanoates by β-oxidation pathway inhibited Pseudomonas putida. *Metabolic Engineering* **2011,** *13* (1), 11-17.

10. Chen, G.-q., A microbial polyhydroxyalkanoates (PHA) based bio- and materials industry. *Chemical Society Reviews* **2009,** *38* (8), 2434-2446.

11. Chen, G.-q.; Wang, Y., Medical applications of biopolyesters polyhydroxyalkanoates. *Chinese Journal of Polymer Science* **2013,** *31* (5), 719-736.

12. Guo-Qiang, C.; Patel, M. K., Plastics derived from biological sources: present and future: a technical and environmental review.(Report). *Chemical Reviews* **2012,** *112* (4), 2082-2099.

13. Chen, G.-Q., *Plastics from Bacteria Natural Functions and Applications*. Berlin, Heidelberg : Springer Berlin Heidelberg: 2010.

14. Burk, M., Sustainable production of industrial chemicals from sugar. *International Sugar Journal* **2010,** *112*, 30-35.

15. Minh, D. P.; Besson, M.; Pinel, C.; Fuertes, P.; Petitjean, C., Aqueous-Phase Hydrogenation of Biomass-Based Succinic Acid to 1,4-Butanediol Over Supported Bimetallic Catalysts.(Report). *Topics in Catalysis* **2010,** *53* (15 18), 1270.

16. Yuan, G. Z.; Tian, J.; Xu, L.; Tang, P.; B, C. D.; W, X. G., Fermentative production of PDO from glycerol by Aspergillus. *Food Ferment Ind* **2006,** *32* (1), 49-52.

17. Huang, Y.; Li, H.; Huang, X.; Yu, Y., Advances of Bio-ethylene. *Chinese Journal of Bioprocess Engineering* **2008,** *6*, 1-6.

18. Tsao, U.; Zasloff, H. B. Production of ethylene from ethanol. 1979.

19. Shota, A.; Taizo, H.; James, C. L., Non-fermentative pathways for synthesis of branched-chain higher alcohols as biofuels. *Nature* **2008,** *451* (7174), 86.

20. Luo, X.; Tang, D.; Li, M., Quantum investigation on the mechanism of isomerization of 1-butylene catalyzed by Rh-complex. *Journal of Molecular Structure: THEOCHEM* **2005,** *731* (1), 139-147.

21. Li, X.; Guan, J.; Zheng, A.; Zhou, D.; Han, X.; Zhang, W.; Bao, X., DFT studies on the reaction mechanism of cross-metathesis of ethylene and 2-butylene to propylene over heterogeneous Mo/HBeta catalyst. *Journal of Molecular Catalysis. A, Chemical* **2010,** *330* (1), 99-106.

22. Shen, L.; Patel, M. K., Life Cycle Assessment of man-made cellulose fibres. **2010**.

23. Ryan, C., Biobutanol potential for bio-based monomers and polymers. In *Emerging Trends in Single and Multi-Use Plastic Packaging,* Atlanta, GA, 2010.

24. Nasiri, M.; Reineke, T. M., Sustainable glucose-based block copolymers exhibit elastomeric and adhesive behavior. *Polym. Chem.* **2016,** *7* (33), 5233-5240.

25. Drumright, R. E.; Gruber, P. R.; Henton, D. E., Polylactic Acid Technology. *Advanced Materials* **2000,** *12* (23), 1841-1846.

26. Wanamaker, C. L.; Leary, L. E.; Lynd, N. A.; Hillmyer, M. A.; Tolman, W. B., Renewable-resource thermoplastic elastomers based on polylactide and polymenthide. *Biomacromolecules* **2007,** *8* (11), 3634.

27. Hillmyer, M. A.; Tolman, W. B., Aliphatic polyester block polymers: renewable, degradable, and sustainable. *Accounts of chemical research* **2014,** *47* (8), 2390.

28. Ding, K.; John, A.; Shin, J.; Lee, Y.; Quinn, T.; Tolman, W. B.; Hillmyer, M. A., High-Performance Pressure-Sensitive Adhesives from Renewable Triblock Copolymers. *Biomacromolecules* **2015,** *16* (8), 2537.

29. Lee, S.; Yuk, J. S.; Park, H.; Kim, Y.-W.; Shin, J., Multiblock Thermoplastic Elastomers Derived from Biodiesel, Poly(propylene glycol), and l -Lactide. *ACS Sustainable Chemistry & Engineering* **2017,** *5* (9), 8148-8160.

30. Xu, X.; Lin, J.; Cen, P., Advances in the Research and Development of Acrylic Acid Production from Biomass 1 1 Supported by the Special Funds for Major State Basic Research Program of China (973 Program, No.2004CCA05500). *Chinese Journal of Chemical Engineering* **2006,** *14* (4), 419-427.

31. Nexant, From Diapers to Paints - Is Bio-Acrylic Acid on the Way? *Prospectus* **2013**.

32. Voelker, F.; Figge, R.; Soucaille, P. Use of sucrose as substrate for fermentive production of 1,2-propanediol. EP2346999B1, 2013.

33. Cameron, D. C.; Altaras, N. E.; Hoffman, M. L.; Shaw, A. J., Metabolic Engineering of Propanediol Pathways. *Biotechnology Progress* **1998,** *14* (1), 116-125.

34. Altaras, N. E.; Cameron, D. C., Enhanced Production of (R)-1,2-Propanediol by Metabolically Engineered Escherichia coli. *Biotechnology Progress* **2000,** *16* (6), 940-946.

35. Fischer, R. H.; Pinkos, R.; Stein, F. Method for producing 1,6-hexanediol and 6-hydroxycaproic acid or their esters. 2002.

36. Theodore, H.; Tatum, H. W. Process for producing hexamethylenediamine from 1-6-hexanediol. 1966.

37. Teruyuki, N.; Wada, M.; Mizuta, H. Preparation process of aliphatic isocyanate. 1992.

38. Papa, A. J.; Kaiser, S. W. Preparation of isophorone and misityl oxide from acetone. 1985.

39. Pascault, J.-P.; Williams, R. J. J., Concepts about Epoxy Polymers, in Epoxy Polymers: New Materials and Innnovations. Wiley-VCH Verlag GmbH & Co.: 2010.

40. Li, Y.; Xiao, F.; Moon, K.; Wong, C., Novel curing agent for lead-free electronics: Amino acid. *Journal of Polymer Science Part a-Polymer Chemistry* **2006,** *44* (2), 1020-1027.

41. Pascault, J.-P.; Williams, R. J. J., Chap 1. General Concepts about Epoxy Polymers in Epoxy Polymers. *Epoxy Polymers: New Materials and Innovation* **2010**, 4.

42. Hsiao, K.; Alms, J.; Advani, S., Use of epoxy/multiwalled carbon nanotubes as adhesives to join graphite fibre reinforced polymer composites. *Nanotechnology* **2003,** *14* (7), 791-793.

43. Chortis, D. I., Structural Analysis of Composite Wind Turbine Blades. **2013,** *1*, 1--8.

44. Alapati, S.; Thomas, M., Influence of nano-fillers on electrical treeing in epoxy insulation. *Iet Science Measurement & Technology* **2012,** *6* (1), 21-28.

45. Epoxy coating market analysis by product by application and segment forecasts to 2024. (accessed September 25).

46. Epoxy Resin Market Projected To Reach $14.26 Billion By 2024. (accessed October 4).

47. Ehrler, S., The compatibility of epoxy-based printed circuit boards with lead free assembly. *Circuit World* **2005,** *31* (4), 3-13.

48. Masterbond EP62-1 Product Information.

49. Masterbond UV25 Product Information.

50. Baroncini, E.; Yadav, S.; Palmese, G.; Stanzione, J., Recent advances in bio-based epoxy resins and bio-based epoxy curing agents. *Journal of Applied Polymer Science* **2016,** *133* (45).

51. Inoue, K.; Sakamoto, T.; Min, J.; Todoroki, K.; Toyo'oka, T., Determination of dicyandiamide in infant formula by stable isotope dilution hydrophilic interaction liquid chromatography with tandem mass spectrometry. *Food Chemistry* **2014,** *156*, 390-393.

52. Smith, I.; Schallenberg, M., Occurrence of the agricultural nitrification inhibitor, dicyandiamide, in surface waters and its effects on nitrogen dynamics in an experimental aquatic system. *Agriculture Ecosystems & Environment* **2013,** *164*, 23-31.

53. Ohshima, S.; Shibata, T.; Sasaki, N., Subacute toxicity of an amine-curing agent for epoxy resin. *Sangyo Igaku* **1984,** *26* (3), 197-204.

54. Bastian, P., Occupational hepatitis caused by methylenedianiline. *Medical Journal of Australia* **1984,** *141* (8), 533-535.

55. Fishback, T.; McMillinl, C.; Farona, M., A new, non-toxic, curing agent for synthetic polyolefins. *Biomedical Materials Engineering* **1992,** *2* (2), 83-87.

56. Stemmelen, M.; Lapinte, V.; Habas, J.; Robin, J., Plant oil-based epoxy resins from fatty diamines and epoxidized vegetable oil. *European Polymer Journal* **2015,** *68*, 536-545.

57. Jaillet, F.; Darroman, E.; Ratsimihety, A.; Auvergne, R.; Boutevin, B.; Caillol, S., New biobased epoxy materials from cardanol. *European Journal of Lipid Science and Technology* **2014,** *116* (1), 63-73.

58. Hu, F., Preparation and Characterization of Fully Furan-Based Renewable Thermosetting Epoxy-Amine Systems. **2015**, 1441--1446.

59. Fache, M.; Monteremal, C.; Boutevin, B.; Caillol, S., Amine hardeners and epoxy cross-linker from aromatic renewable resources. *European Polymer Journal* **2015,** *73*, 344-362.

60. Takahashi, T., Biocomposites Composed of Epoxidized Soybean Oil Cured with Terpene-Based Acid Anhydride and Cellulose Fibers. **2008**.

61. Metkar, P.; Scialdone, M.; Moloy, K., Lysinol: a renewably resourced alternative to petrochemical polyamines and aminoalcohols. *Green Chemistry* **2014,** *16* (10), 4575-4586.

62. Motahari, A, On the Thermal Degradation of a Novel Epoxy- Based Nanocomposite Cured With Tryptophan as an Environment-Friendly Curing Agent On the Thermal Degradation of a Novel Epoxy- Based Nanocomposite Cured With Tryptophan as an Environment-Friendly Curing Agent. **2015,** *2348* (June 2017).

63. Ma, S.; Webster, D., Naturally Occurring Acids as Cross-Linkers To Yield VOC-Free, High-Performance, Fully Bio-Based, Degradable Thermosets. *Macromolecules* **2015,** *48* (19), 7127-7137.

64. Jaillet, F.; Desroches, M.; Auvergne, R.; Boutevin, B.; Caillol, S., New biobased carboxylic acid hardeners for epoxy resins. *European Journal of Lipid Science and Technology* **2013,** *115* (6), 698-708.

65. Stanzione, J.; La Scala, J., Sustainable Polymers and Polymer Science: Dedicated to the Life and Work of Richard P. Wool. *Journal of Applied Polymer Science* **2016,** *133* (45).

66. FDA, CFR - Code of Federal Regulations Title 21. **2015,** *3* (2), 25 -26.

67. Koupantsis, T.; Pavlidou, E.; Paraskevopoulou, A., Glycerol and tannic acid as applied in the preparation of milk proteins - CMC complex coavervates for flavour encapsulation. *Food Hydrocolloids* **2016,** *57*, 62-71.

68. Shibata, M.; Nakai, K., Preparation and Properties of Biocomposites Composed of Bio-Based Epoxy Resin, Tannic Acid, and Microfibrillated Cellulose. *Journal of Polymer Science Part B-Polymer Physics* **2010,** *48* (4), 425-433.

69. Wei, L., Online Determination of Trace Amounts of Tannic Acid in Colored Tannery Wastewaters by Automatic Reference Flow Injection Analysis. *Journal of Automated Methods & Management in Chemistry* **2010**.

70. Lau, S.; Wahn, J.; Schulz, G.; Sommerfeld, C.; Wahn, U., Placebo-controlled study of the mite allergen-reducing effect of tannic acid plus benzyl benzoate on carpets in homes of children with house dust mite sensitization and asthma. *Pediatric Allergy and Immunology* **2002,** *13* (1), 31-36.

71. Sigma-Aldrich Tannic Acid ACS Reagent. http://www.sigmaaldrich.com/catalog/product/sial/t0125?lang=en&region=US (accessed August 3).

72. Sigma-Aldrich Dicyandiamide. http://www.sigmaaldrich.com/catalog/product/aldrich/d76609?lang=en&region=US (accessed August 3).

73. Sigma-Aldrich 4,4'-Diaminodiphenyl sulfone. http://www.sigmaaldrich.com/catalog/product/mm/821073?lang=en&region=US (accessed August 9).

74. Shibata, M.; Teramoto, N.; Makino, K., Preparation and Properties of Biocomposites Composed of Epoxidized Soybean Oil, Tannic Acid, and Microfibrillated Cellulose. *Journal of Applied Polymer Science* **2011,** *120* (1), 273-278.

75. Fei, X.; Wei, W.; Zhao, F.; Zhu, Y.; Luo, J.; Chen, M.; Liu, X., Efficient toughening of epoxy-anhydride thermosets with a biobased tannic acid derivative. *Acs Sustainable Chemistry & Engineering* **2017,** *5* (1), 596-603.

76. Fei, X.; Zhao, F.; Wei, W.; Luo, J.; Chen, M.; Liu, X., Tannic Acid as a Bio-Based Modifier of Epoxy/Anhydride Thermosets. *Polymers* **2016,** *8* (9).

77. Aldrich, S., Product Specification: Tannic Acid - ACS Reagent. 2017; p 1.

78. Pacific, G., Safety Data Sheet: GP 2074 Phenolic Epoxy Hardener. 2015; pp 1-12.

79. Chemtrec, Material Safety Data Sheet: Tannic Acid. 2017; pp 1-6.

80. Mendis, G.; Weiss, S.; Korey, M.; Boardman, C.; Dietenberger, M.; Youngblood, J.; Howarter, J., Phosphorylated Lignin as a Halogen-Free Flame Retardant Additive for Epoxy Composites. *Green Materials* **2016,** *4* (4).

81. Xia, Z.; Singh, A.; Kiratitanavit, W.; Mosurkal, R.; Kumar, J.; Nagarajan, R., Unraveling the mechanism of thermal and thermo-oxidative degradation of tannic acid. *Thermochimica Acta* **2015,** *605*, 77-85.

82. Shechter, L.; Wynstra, J., Glycidyl ether reactions with alcohols, phenols, carboxylic acids, and acid anhydrides. *Industrial and Engineering Chemistry* **1956,** *48* (1), 86-93.

83. Margem, F.; Monteiro, S.; Neto, J.; Rodriguez, R.; Soares, B., The dynamic-mechanical behavior of epoxy matrix composites reinforced with ramie fibers. *Materia-Rio De Janeiro* **2010,** *15* (2), 167-175.

84. Shimasaki, T.; Yoshihara, S.; Shibata, M., Preparation and properties of biocomposites composed of sorbitol-based epoxy resin, pyrogallol-vanillin calixarene, and wood flour. *Polymer Composites* **2012,** *33* (10), 1840-1847.

85. Thirukumaran, P.; Parveen, A.; Sarojadevi, M., Synthesis of eugenol-based polybenzoxazine-POSS nanocomposites for low dielectric applications. *Polymer Composites* **2015,** *36* (11), 1973-1982.

86. Produktions, E., Medical-grade epoxy features high glass transition temperature. *Sealing Technology* **2013,** *2013* (11), 4--5.

87. Yi, J.; Um, M.; Byun, J.; Lee, S.; Lee, S., Development of high Tg epoxy resin and mechanical properties of its fiber-reinforced composites. *Journal of Applied Polymer Science* **2013,** *127* (6), 4328-4333.

88. Bergum, E., Thermal Analysis of Base Materials Through Assembly: can current analytical techniques predict and characterize differences in laminate performance prior to exposure to thermal excursions during assembly? *Printed Circuit Design and Manufacture* **2003**.

89. Materials, H. A., Technical Datasheet - Aradur® 9664-1. 2015; pp 1-3.

90. Morgan, R.; Mones, E., The Cure Reactions, Network Structure, And Mechanical Response Of Diaminodiphenyl Sulfone-Cured Tetraglycidyl 4,4'diaminodiphenyl Methane Epoxies. *Journal of Applied Polymer Science* **1987,** *33* (4), 999-1020

4. ACETYLATED TANNIC ACID: A BIO-BASED ALTERNATIVE TO BROMINATED FLAME RETARDANTS IN EPOXY

This work is to be submitted to a journal at a later date. It is based off of work that I performed in collaboration with Natalie Burgos, an undergraduate researcher. Natalie performed the TGA of samples within epoxy and assisted me with running the FR samples at FPL during which we received mentorship on from Mark Dietenberg. However, I wrote the text and performed the data analysis on my ow while receiving intellectual input and mentorship from the collaborators on the work.

4.1 Introduction

For the past several decades, halogenated flame retardants (HFRs) have been used as additives in a variety of different polymer systems in order for these materials to meet the stringent flame retardant (FR) standards required in the US and UK.[1] HFRs are prevalent throughout the world in a variety of applications including pentabromodiphenyl ether (PentaBDE) in furniture,[2] hexabromocyclododecane (HBCD) in building insulation,[3] and 1,2,3-trichloro-4-(2,3,4-trichlorophenyl)benzene (Aracor) and tetrabromobisphenol A (TBBPA) in the printed circuit boards of electronics.[4] However, more recent research has shown that bioaccumulation of HFRs in humans can lead to lower birth weight and length of children,[5] impair neurological development,[5] and even cause cancer.[6, 7] Furthermore, the health impacts of halogenated flame retardants are felt more strongly in less-wealthy regions of the world where individuals are found to have elevated concentrations of HFRs in breast milk and water.[8] Due to these concerns, there is currently a high demand in industry for alternative chemicals to HFRs in a variety of industries such as automotive, electronics, and construction.[9]

For these reasons, there has been a significant amount of research on biologically based flame retardant additives, such as cellulose,[10] deoxyribonucleic acid,[11, 12] lignins,[13] condensed tannins and tannic acid[14-18] but these compounds are often limited in application by a solubility mis-match between compounds and hydrophobic polymer systems, such as epoxy. There are several methods that have been used to circumvent this challenge Surfactant can be used to assist dispersion and increase the overall dispersion of the additive,[19, 20] but excess surfactant can effect the resulting thermomechanical properties such a T_g – which are of vital importance for most applications.

Using solvent has been found to greatly increase dispersion of these additives in polymers,[21] but will also lead to the environmental emission of volatile organic compounds. Chemically modifying the additive to better match the system into which it is being inserted can increase the interfacial compatibility of the additive and the polymer matrix[22] but can potentially make the product more difficult to commercialize due to the added chemical steps in manufacturing. An additional concern with this method is that many of the reactants are synthesized from petroleum, which is a non-renewable resource, and the synthesis pathways can involve toxic compounds.

There is a need for exploration of these and many other processing mechanisms to enable the dispersion of such biologically-sourced molecules into hydrophobic polymer systems. However, there is very limited research in this topic for several bio-based chemicals above, especially TA. TA is a natural polyphenolic compound found in nuts, galls, seeds, and tree bark that is commercially available for purchase at a similar or cheaper cost than commercially available flame retardant additives. TA is a hydrolysable tannin that – when dispersed into polymer matrices – has been found to enhance the thermal properties of plastics.[23] When thermally-activated in the presence of a fire, TA was found to crosslink into the polymer network forming a char barrier between the surface of the material and the propagating flame therefore retarding the spread of the fire[21]. Because of this, TA has been explored as a FR additive in a variety of polymer matrices including poly(lactic acid),[14, 15] nylon 6,[23, 24] polyesters,[25] and urethane foams.[26] TA shows favorability for use as a BFR and PPC alternative compound, but its limited dispersibility in epoxy is the main barrier to its use in this application. Uniform dispersion of high amounts of TA in epoxy has only recently been achieved but demands very high temperature and long timescales.[27-29]

Although TA shows promise as an environmentally-sourced flame retardant alternative chemical in epoxy systems, researchers have had limited success with it in practice. In order to combat this, researchers have performed chemical functionalization to better match TA to hydrophobic polymer systems and simultaneously increase its flame retardant potential. Previous work identified that surface modification of TA using epoxy resin could increase the compatibility of the molecule; however, the dispersion of up to 8 wt% TA by this method did not increase the flame retardancy of the composite significantly.[27, 28] Additionally, others have used this same chemical reaction between TA and epoxy rings to functionalize the molecule with hydrophobic carbon chains to enhance dispersion, but again flame retardancy was limited.[27] Other researchers have used transesterified the molecule to increase its hydrophobicity and flame retardancy in nylon and PLA systems.[28] Even slight degrees of modification of the molecule showed drastic changes in solubility, as slightly-modified molecules were no longer soluble in water. Varying the degree of functionalization from low to high-esterification showed very little change in the compatibility output. Researchers showed that acetylation of TA increased its flame retardancy in nylon and PLA, but no researchers have studied how acetylation of TA affected its flame retardancy in epoxy thermosets.

The goal of this study was to chemically functionalize TA by performing a trans-esterification of TA using acetic anhydride (AA) and test the ability of this material to improve compatibility and flame retardancy in epoxy. TA was acetylated to different degrees by adding AA at varying molar ratios of acetate group on AA to phenol group on TA. The resulting acetylated TA molecules were dispersed in epoxy at varying weight percentages. The resulting materials were found to have increased flame retardancy as compared to TA control samples which had not been modified. Additionally, the flame retardant ability of the additives was dependent on the degree of acetylation. The results from this work indicate the potential for acetylated TA to be used as a cheap, environmentally-sourced HFR and PPP alternative chemical.

4.2 Methods

4.2.1 Materials

TA, AA, 1 methyl-imine, and 2-pentanone were purchased from Sigma Aldrich (St. Louis, MO, USA). EPON 825 (DGEBA) resin was purchased from Hexion, Inc. (Louisville, KY, USA). Mold Max 60 silicone precursor and initiator (parts A and B) were purchased from Smooth-On, Inc. (Macungie, PA, USA) GP2074 novolac resin was purchased from Georgia Pacific (Atlanta, GA, USA). 20mL borosilicate scintillation vials were purchased from Thermo Fisher Scientific (Waltham, MA, USA). Poly(tetra fluoroethylene) magnetic stir bars were purchased from Carolina Biological Supply Company (Burlington, NC, USA). All materials were used as received.

4.2.2 Preparation of acetylated TA powders

Acetylation of TA was performed based on a synthesis pathway determined from previous literature.[14, 15] Tannin, acetic anhydride, and 1-methylimidazole (1wt% on TA) were combined in a 100 mL round bottom flask sealed with a rubber septum. Acetic anhydride was added at varying molar ratios of acetyl groups to galloyl groups (A:G) to ensure differences in chemical modification between powders (Table 1). For this work, the molar weight of TA was assumed to be 1701.1 g/mol as this has been used in previous literature.[28, 29] Additionally, the amount of phenol groups per TA and acetyl groups per AA were assumed to be 25 and 2 respectively.[14, 28, 29]

For this work molar ratios (α) of 0.25, 0.5, 0.75, 1, and 5 were studied. Nitrogen gas was fed into the flask by penetrating the septum with a needle connected to a nitrogen line. Another needle was pierced through to allow for out-flow of the nitrogen gas. The mixture was heated at 65°C for 4 hours in a nitrogen atmosphere. After reaction, the contents of the vial were added dropwise to a vigorously stirring 500mL beaker of distilled water containing distilled-water based ice cubes. The suspension was centrifuged and the pH of the supernatant was measured and then the solution was discarded. This process was repeated until the supernatant achieved pH of 4. The powders were dried in vacuum at 40°C. Composite Positive Mold Preparation for Plaques and Bars

A 3D design of a composite block was created using Fusion 360 to make the necessary silicone molds. A ramp on the side of each mold was included that serves as a starting point when taking silicone out of the mold to prevent ripping the silicone. About ½ inch of space on each side of each positive mold was created, and about ¼ inch on top of the mold was designed to create the bottom for the silicone mold to be generated later. A CAM process in Fusion 360 used to machine all the corners on the composite using a sheet router. An orbital sander was used to sand down the top surface of each plaque or bar using 220 grit sandpaper. This allowed silicone to separate from the composite positive mold more easily, and the epoxy to separate more easily from the silicone negative mold later. The mold was sprayed with air to remove any unwanted composite dust.

4.2.3 Epoxy Sample Preparation

Silicone molds were prepared by machining composite “master” blocks and casting Mold Max-60 Silicone Rubber Compound (Smooth-On, Inc.) around the block with subsequent demolding. to create the mold cavity. The silicone mold was allowed to cure for at least 12 hours at room temperature before use. The silicone negative molds for each batch of epoxy were prepared by spraying with mold release (Stoner E-206 Silicone Mold Release), heating for five minutes at 80°C then spraying again. The TA powders were added to EPON 825 resin and mechanically mixed using a Flacktek mixer (SpeedMixer, Landrum, SC, USA) for several minutes at 1250 rpm. After mixing, TETA was added in a ratio of 14 parts per 100 parts EPON 825. The resulting mixture was then mechanically mixed for several additional minutes at 1250 rpm to properly disperse TETA into the solution. The solutions were then poured into the silicone molds and put in a vacuum chamber to remove residual bubbles from pouring and mixing. The result was set overnight at room temperature. The following day, samples were removed from silicone molds and put into an oven at room temperature where they were then heated at 5°C/min to 100°C for 2 hours to cure and then heated at a 5°C/min rate to 125° to be post-cured for 2 additional hours.

4.2.4 Epoxy Sample Characterization

Optical Microscopy was performed using a Zeiss optical microscope (Zeiss, Thornwood, NY, USA). Samples were prepared by pouring 5 mL of sample onto a microscope slide. Spacers were used on either side of the sample to ensure consistent sample thickness and a microscope slide was placed on top. Image analysis was done using ImageJ (National Institute of Health, Bethesda, MD, USA).

Attenuated total reflectance (ATR) Fourier transform infrared (FTIR) spectroscopy was performed using a PerkinElmer Spectrum 100 FTIR Spectrometer (PerkinElmer, Seer Green, Beaconsfield, UK) outfitted using a zinc selenide (ZnSe) crystal. Samples were scanned from 650 cm$_{-1}$ to 4000 cm$_{-1}$ in transmissive model. Epoxy samples of thickness 0.35 cm containing the powders as additives at 10 wt% and peaks were normalized to a control epoxy sample. These samples were not cured as above but were instead set at room temperature to avoid reaction between TA and epoxy resin. Samples were scanned 4 times and normalized to the phenyl peak at 1605 cm$_{-1}$ using Spectra (PerkinElmer, Seer Green, Beaconsfield, UK). Three samples were analyzed for each powder. Absorbance values were calculated using Spectra (PerkinElmer, Seer Green, Beaconsfield, UK) and were averaged between samples.

Ultraviolet-visible (UV/Vis) spectroscopy was performed using a Lambda 950 UV-VIS-NIR spectrophotometer (PerkinElmer, Waltham, MA, USA). Three samples at each concentration were prepared in acrylic cuvettes. All absorbance values were normalized to an empty cuvette. Transmission was measured for all wavelengths between 200-800 nm to measure the full visible light spectrum. Transmission curves were analyzed using OriginPro 2019 (OriginLab, Northampton, MA, USA). A UV-flashlight was also used to help characterize samples. An Optimax 365 UV-LED flashlight (Spectroline, Westbury, NY, USA) was pointed at the samples. The photo was taken using a PowerShot A70 Camera (Canon, Woodridge, IL).

Thermogravimetric analysis (TGA) was performed with a Q50 thermogravimetric analyzer (TA Instruments, Newcastle, DE, USA). Samples were prepared for TGA analysis by shaving off 15±2.3 mg of sample from epoxy products. Experiments were performed in nitrogen with a 60 mL/min flow rate using a 20 °C/min heating rate from 30 °C to 900 °C. Three epoxy samples were run at each concentration and results were averaged. T_d was determined by finding the peak of the mass loss rate curve using Universal Analysis (TA Instruments, Newcastle, DE, USA) and averaging the temperature values at this point. Remaining char values were calculated by measuring the weight fraction of the sample using Universal Analysis (TA Instruments, Newcastle, DE, USA) at the completion of the TGA test (800 °C) and then averaging the weight fraction values at this point.

Differential Scanning Calorimetry (DSC) was performed on liquid pre-polymer samples using a Q2000 Differential Scanning Calorimeter (TA Instruments, Newcastle, DE, USA). Samples of 12±1.2 mg were loaded into aluminum pans and measured using a heat/cool/heat cycle from – 75 °C to 200°C with a heating and cooling rate of 25 °C/min. Three samples were measured at each concentration and the mean glass transition value of the second heat curve was calculated as the midpoint of the incline observed on thermograms and averaged for each concentration using Universal Analysis (TA Instruments, Newcastle, DE, USA).

Dynamic Mechanical Analysis (DMA) was performed on all samples using Q800 Dynamic Mechanical Analyzer (TA Instruments, Newcastle, DE, USA). Samples were prepared of dimensions 5.5 cm x 1.2 cm x 0.35 cm by pouring prepared solutions into silicone molds and then cured. Samples were polished to remove remaining silicone from their surfaces. A dual cantilever mechanical test was performed at a frequency of 1 Hz and displacement of 0.15 µm. Temperature was held constant at 30 °C and the storage modulus was measured for 20 minutes. Three samples were measured at each TA concentration and were averaged. E' values were calculated by averaging the datapoints for all samples of the same wt%. TA using Universal Analysis (TA Instruments, Newcastle, DE, USA).

Mechanical testing was performed using a compression fixture on a mechanical testing frame (MTS Instruments, Eden Prairie, MN, USA). Cylindrical samples were prepared with dimensions of 24.2 ± 1.3 mm X 30.1 ± 4.8 mm being diameter and height respectively. Five samples were measured at each concentration and they were loaded to break, which was determined by observable cracking and fracture on the surface of the part. Toughness values were obtained by integrating the stress/strain curves using OriginPro 2017 (OriginLab Inc., Northampton, MA, USA).

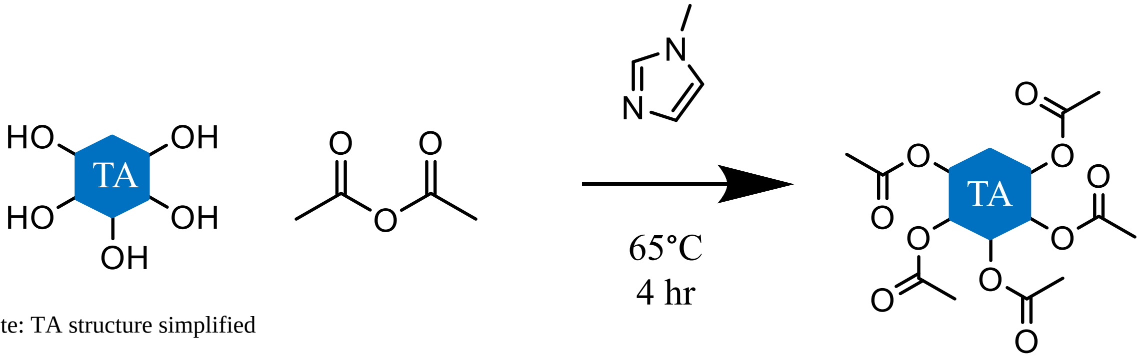
Mass loss calorimetry (MLC) was performed using an MLC 2004 mass loss calorimeter (Fire Testing Technologies, East Grinstead, UK) which was modified with a chimney and additional thermopiles. The procedure determined by Mendis et. al was performed.[13] Poly(methyl methacrylate), polystyrene, and ethylene glycol standards were used to calibrate the instrument. The heat source was set at 35 kW/m^2 and remained constant for the duration of the test. A spark igniter was used to ignite the samples. The test was concluded when the mass loss rate was less than 2.5 g/min. Five specimens were analyzed for each composition and were prepared according to ASTM E 2102-15. Mass loss curves were analyzed using OriginPro software.

Statistical analysis was performed using JMP (SAS Institute, Cary, NC, USA). A student's t-test was run to compare samples. A p-value <0.05 was used to indicate statistically significant differences between samples. Regression analysis was performed using OriginPro 2017 (OriginLab Inc., Northampton, MA, USA). Results were fit to an exponential decay and linear models, and the reported equations and standard error (S_e) values were output by the software after regression analysis. S_e values <0.05 were determined as appropriate fits for the regression.

4.3 Results and Discussion

4.3.1 Preparation of Flame Retardant Additives:

Acetylation of TA was performed by using procedure developed by previous researchers.[14] The synthesis pathway can be visualized (Figure 4.1).



Note: TA structure simplified

Figure 4.1: Reaction sceme for the reaction of TA and AA.

Table 4.1: Yields of the reactions between TA and AA.

Molar Fraction (acetyl / galloyl)	Acetic Anhydride Added (grams AA/grams TA)	Reaction Yield (%)
0.25	0.189	10.2 ± 6.1
0.5	0.378	17.5 ± 10.1
0.75	0.568	15.3 ± 9.2
1	0.757	25.2 ± 4.3
5	3.78	84.4 ± 8.1

Reaction yields were calculated and are listed (Table 1). The resulting compatibility changes after chemical modification were not found to significantly change with small molar fractions. Much of the reaction products in the 0.25-1 samples were washed away during the cleaning procedure due to an insignificant change in compatibility in the reaction product. This reaction yield was observed in all samples except the excess anhydride (5) sample which had a significantly increased reaction yield as compared to the other samples. These samples during the washing procedure were largely found to precipitate out, whereas a significantly reduced amount of solid precipitated out in the smaller molar fraction samples.

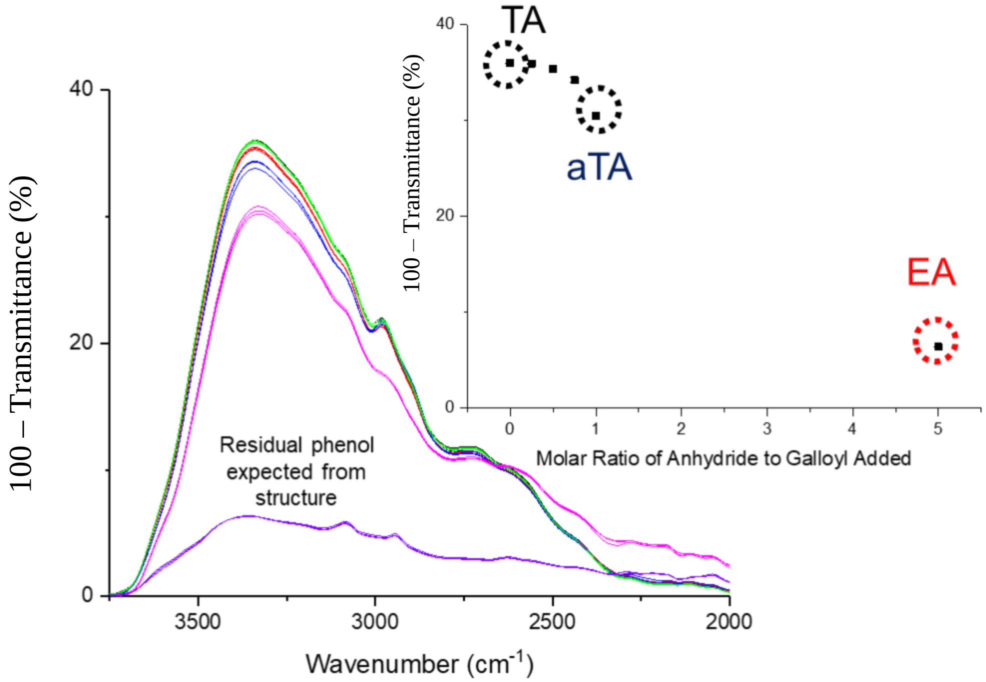


Figure 4.2: FTIR analysis of functionalized TA samples in part a) Phenolic peak on FTIR is analysed after normalization to phenyl stretch on TA (1605 cm^{-1}). Maximum transmittance of the peak was compared for samples part b) shows a decrease in peak. 3 distinct samples are identified on the curve and labeled as TA, aTA, and EA.

Reaction products were then characterized using FTIR analysis (Figure 4.2). Results from FTIR analysis suggest that the degree of functionality was not fully dependent on the ratio of the additives, which was consistent with previous literature (Grigsby 2013). At a 1:1 molar ratio of A:G, it was expected to achieve maximum functionalization. However, the addition of excess anhydride resulted in a reduction of the phenol peak of TA past this point, as evidenced in Figure 1 by the 5:1 sample. The significant reduction in the phenol peak was attributed in this analysis to the addition of acetic anhydride to the outer groups of the “surface” of the molecule and is expected from the chemical synthesis pathway. The FTIR results suggest that the degree of functionality is significantly different in the control, 1, and 5 samples which were labeled TA, aTA, and EA for the purpose of this work. For this reason, further exploration of flame retardancy and material properties were studied for these 3 levels of functionalization of the molecule.

After chemical modification, there was a difference in the appearance of the powders, as TA samples were a tanned color, aTA powders were a light tan, and EA powders were white. Water compatibility measurements were performed to further indicate the changes in chemical structure to TA (Figure 2). TA samples were found to dissolve in water. However, aTA samples slightly dispersed in the water as evidenced by the slightly browned solution color in this case. The majority of the powder precipitated from solution and aggregated at the bottom of the vial. EA samples showed visible changes in compatibility with water as compared to TA powders but additionally remained suspended.

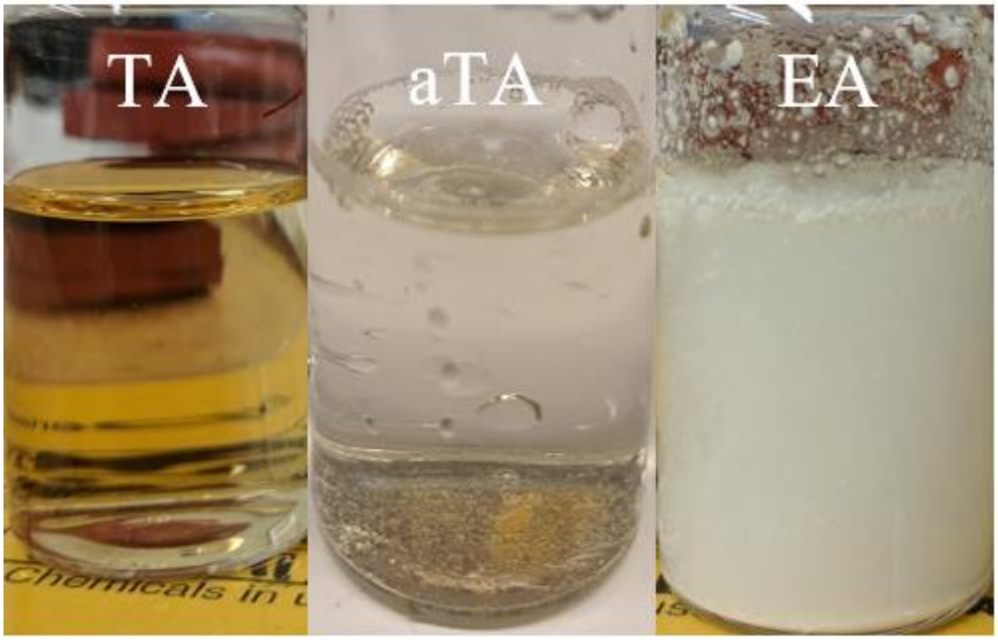


Figure 4.33 wt% TA, aTA and EA powders dispersed in water. Photos show TA dissolved, aTA partly dissolved but also precipitated, and EA did not dissolve into solution but suspended.

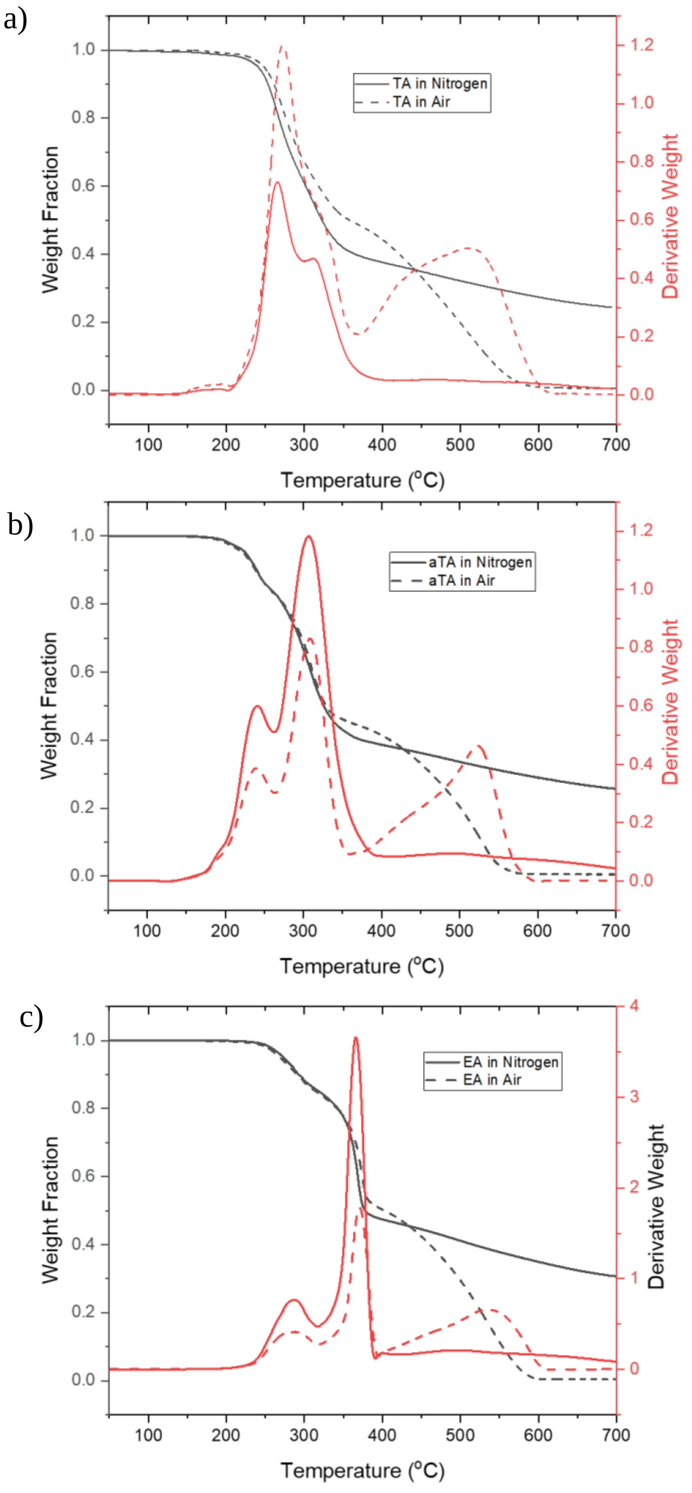


Figure 4.4: TGA of a) TA, b) aTA, and c) EA powders. Results indicate that aTA and EA powders had increased thermal stability as compared to control samples.

The result from FTIR, water solubility, and TGA indicate that the 3 TA samples have distinct chemical functionalities. FTIR peaks indicate that the aTA and EA samples were surface functionalized, as evidenced by the decrease in the magnitude of the phenol peak. Water solubility indicated that the more acetic anhydride that was added to the samples, the more hydrophobic, on average, the samples became. TGA indicated a distinct and unique pathway for each powder with increased thermal stability in the aTA and EA samples, with EA samples having the highest thermal stability. The TGA results also indicate that the degradation pathway of the TA molecule is largely led by the degradation of the phenol groups on the surface of the molecule. However, aTA and EA samples showed that while there was evidence of some residual phenol groups in each sample, the magnitude of this peak decreased as compared to the internal TA structure, further suggesting degree of modification differences between these samples. The bulk of thermal degradation occurred at the temperature associated with the degradation of the internal TA structure in both aTA and EA samples. The result of this section of the work is that it is suggested that this chemical synthesis pathway does in fact functionalize TA with acetic anhydride. A more hydrophobic structure is created, and the degree of hydrophobicity of the molecule is tunable based on the molar ratio of the anhydride group on acetic anhydride to the galloyl group on TA. The addition of acetyl groups to the surface of TA additionally makes the molecule's degradation pathway change resulting in a material with a higher char yield and, in the case of EA samples, a significantly increased temperature of thermal degradation.

This result is not surprising as the addition of acetyl groups to TA has been shown to have this effect. We believe the preliminary explanation of this behavior is that the outermost acetyl groups on aTA and EA are less thermally stable than the internal TA structure, as evidenced by TGA. The breakage of this phenyl ester bond on the acetylated TA results in an increase in the ability of the powder to char resulting in an observable increase in the thermal stability of the material as compared to the control TA sample, which would break the phenol/galloyl bond on the molecule. Partial acetylation of the molecule leaves phenolic hydroxyls available for degradation. The phenol groups do not form a char that is more thermally stable than the control sample, and thus there is no increase in the thermal stability of the char, though there is an observable decrease in the magnitude of the phenol degradation peak on TGA which is a result of fewer free phenolic hydroxyls due to functionalization. The addition of the phenyl ester increases the magnitude of the char yield by delaying phenol degradation and the more phenyl ester that is added to the molecule, the more thermally stable the powder is. Thus, tacetylatedof TA shows promise as a flame retardant additive due to the increase in thermal stability of the resultant molecule.

4.3.2 Measuring Compatibility of Samples

TA, aTA, and EA were dispersed into epoxy resin at different weight percentages and their compatibility was measured. Samples were analyzed using optical microscopy (Figure 4.5).

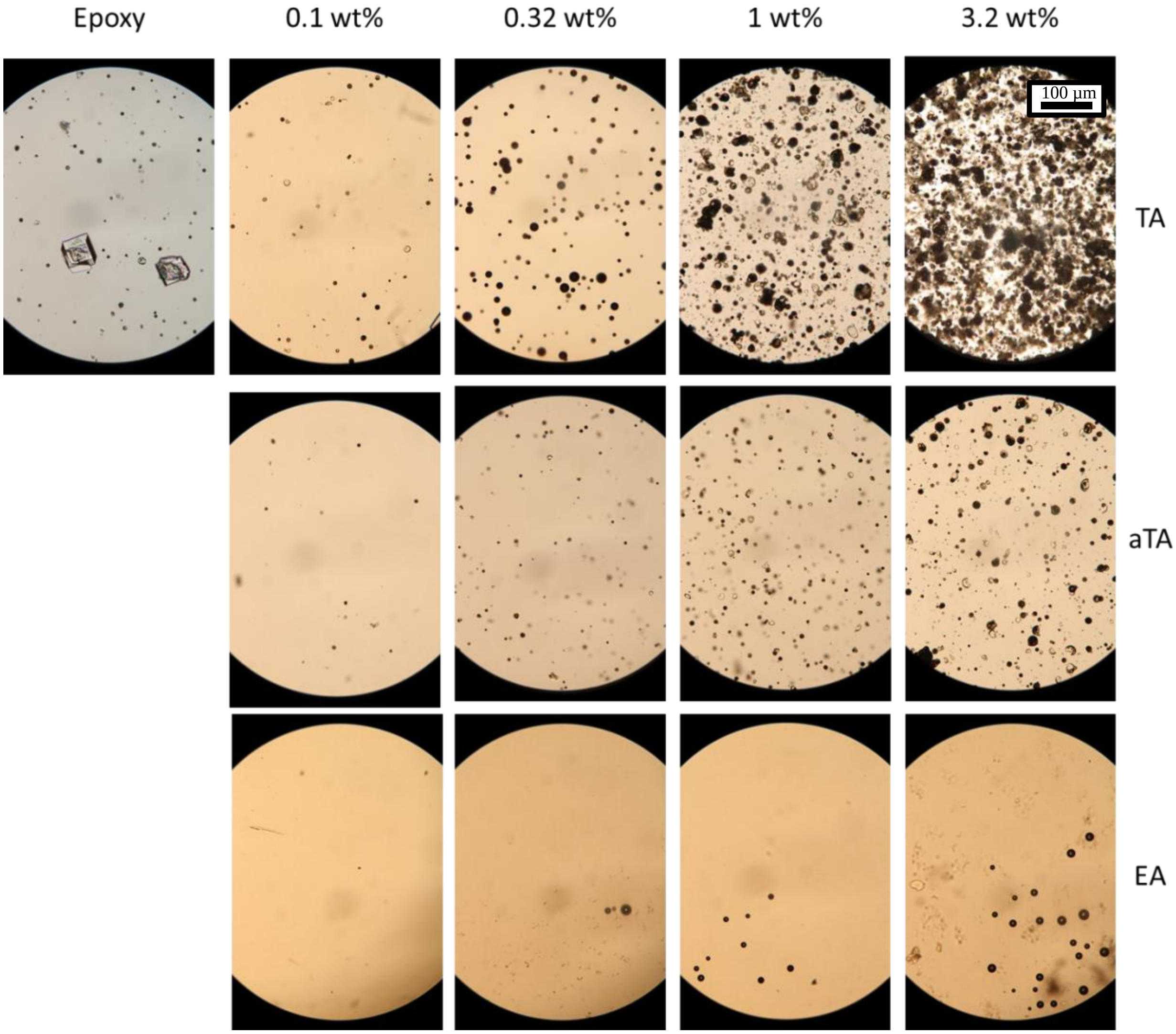


Figure 4.5: Optical microscopy to measure compatibility of powders in epoxy resin (magnification 30X). Results indicate that increased chemical functionalization resulted in increased compatibility.

Samples were found to increase in overall "brown-ness" and opacity as TA loading was increased. While TA did not fully disperse in any of the samples, large clumping was most obviously present to the eye at and above 1 wt% TA in epoxy. aTA samples were found to have increased compatibility as compared to the TA samples, however clumping was observed in the 3.2 wt% sample though the aggregates were significantly smaller in size. EA samples did not have any significant signs of aggregation regardless of loading level; however, all samples were found to be browned as compared to the control resin. Overall, EA samples had the highest degree of compatibility in epoxy, and the compatibility increase was proportional to the amount of acetylation suggested by FTIR.

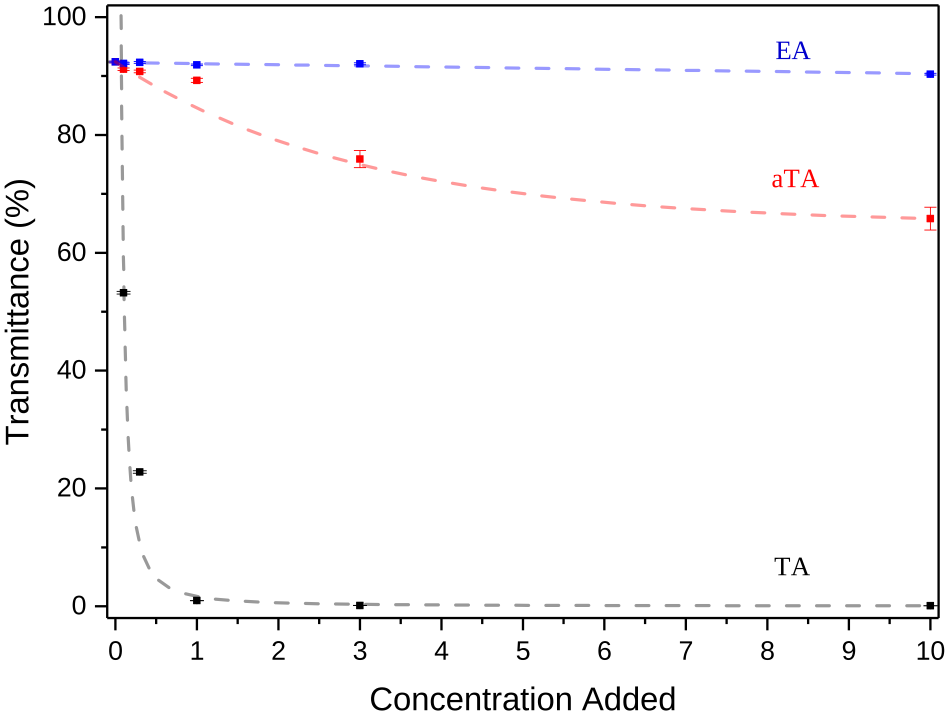


Figure 4.6: Average transmittance data for samples containing FR additives. Trendlines added to help make trends clearer.

The compatibility of the samples was quantified using UV-Vis spectroscopy (Figure 4.6)**.** The results from UV-Vis data showed that TA samples showed significant decreases in transmittance with any addition of TA to the solution to near 0% with the addition of 1 wt% TA. Greater than 1 wt% TA, little change in compatibility was observed between samples loaded up to 10wt%. The aTA samples showed decreased transmittance with addition, though the change was not quite as drastic as what was seen in TA samples. EA samples showed no significant change in transmittance with addition of the powder to the resin, and this trend was found up to 10wt%.

UV-vis spectroscopy and optical microscopy indicated that the solubility limit of TA in epoxy resin was below 1 wt%. As acetylation of the molecule was increased, the compatibility in epoxy increased. aTA samples showed signs of aggregation in epoxy at a comparable weight percent, but the size of these aggregates was significantly decreased. EA samples did not show significant signs of aggregation regardless of the loading level of to 10wt%. The results indicated that degree of acetylation of TA resulted in an increase in compatibility, and the compatibility was tunable based on the degree of acetylation.

4.3.3 Thermal/Thermomechanical Stability

In order to get a better understanding of the thermal stability of the samples, thermogravimetric analysis (TGA) was performed (Figure 4.7). The results indicated that unmodified TA in epoxy showed increased thermal stability in the 0.1, 0.32, and 1 wt.% TA samples but a downward trend in thermal stability past that loading level. The addition of any amount of acetylation of the molecule resulted in a marked, visible increase in the temperature of initiation of thermal degradation and the temperature of the maximum of the derivative weight curve by approximately 50°C in either case. The addition of aTA and EA samples at or past the 1 wt% loading level resulted in a notch on the derivative weight curve at approximately 430_{o}C. These results suggest that the resulting char of acetylated TA samples was more thermally stable in nitrogen than the control or TA samples.

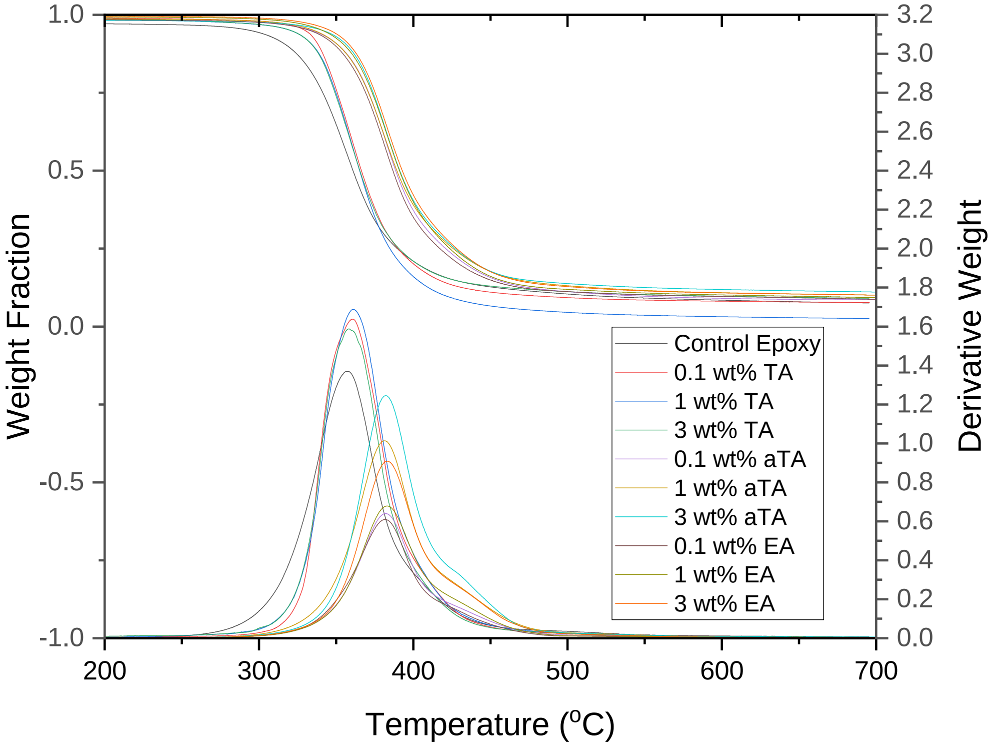


Figure 4.7: TGA of TA, aTA, and EA samples in epoxy in nitrogen. Results indicate all aTA and EA samples had increased thermal stability as compared to control samples. Additionally, all samples formed a stable char at elevated temperature.

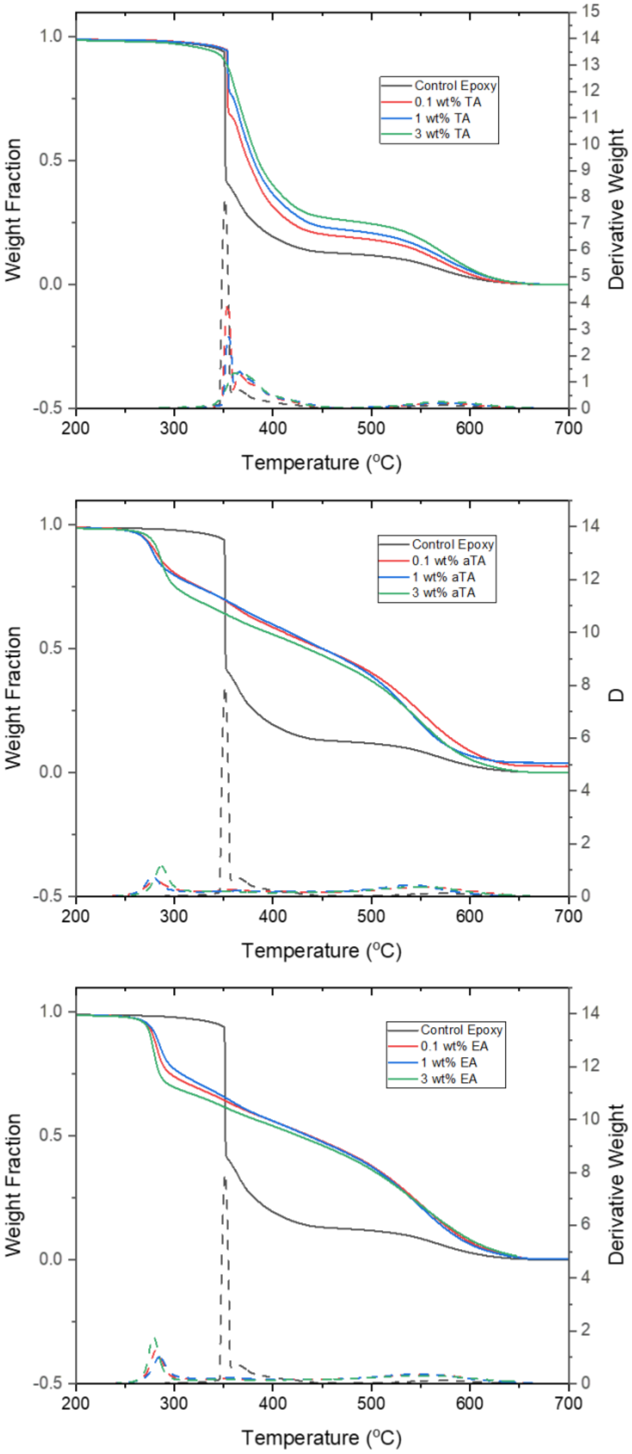


Figure 4.8: Thermogravimetric Analysis of Samples in Compressed Air. Results from this test indicate that TA samples are medicated by the degradation of epoxy whereas aTA and EA samples degrade with the powders and then form a more stable char.

Samples were additionally characterized by TGA with compressed air to help better anticipate the flame-retardant behavior of the samples (Figure 4.8). Thermal degradation in compressed air indicated that TA samples, regardless of loading level, did not significantly change the thermal degradation temperatures of the samples. However, with increased TA loading, the amount of char remaining at 500°C increased. This indicated that the presence of TA in the samples increased the thermal stability of the resulting char, a behavior seen for TA previously for other materials in the literature.[15, 16] The TA-containing samples did not thermally degrade at the temperature associated with TA molecular degradation. Instead, all samples showed indication of thermal degradation at the temperature of the epoxy thermoset, but the amount of char remaining at 500°C was dependent on the TA loading, as increased TA loading resulted in more char.

These results suggest that the degradation of the thermoset network, and not TA itself, is what initiates thermal degradation of the composite material in TA-epoxy composites. Unmodified TA has been found to crosslink into epoxy thermosets at temperatures above 100°C (cite). The resulting crosslinked TA-epoxy material traditionally shows thermal degradation at around 525°C, which was not found in the material for this study. In this present study, the thermoset was crosslinked with TETA at room temperature. After this, the resulting thermoset is further cured at 100°C and 125°C for 1 and 2 hours respectively. During this post-cure, the TA additives could crosslink into the system with any remaining unreacted epoxy groups. The results from this study indicate that TA does crosslink into the system but does not *fully* crosslink into the system. This is expected because the amine gets the first chance to react at room temperature resulting in less availability for TA to crosslink into the system. For this reason, TA molecule is chemically bound to the network itself resulting in a material that is epoxy-thermoset dependent for thermal degradation, as indicated by TGA in both nitrogen and air. TA has been found to significantly increase char yield when used as an additive for a variety of polymer matrices. The reason for this behavior is believed to be because of the high density of phenyl groups within the molecule which are able to form a dense, highly-thermally stable char. This result was observed for all TA-containing samples. As TA loading was increased the ability for the material to char increased as well. The preliminary explanation for this behavior is that more TA in the sample results in more phenyl groups. The crosslinked char then thermally degrades at approximately 575°C regardless of TA loading level.

Chemically modified (aTA and EA) samples had a significantly altered thermal degradation pathway as evidenced by TGA in both nitrogen and compressed air. EA and aTA samples showed thermal degradation at 275°C which resulted in a char that was more thermally stable than the control epoxy sample. This thermal degradation peak was not significantly different than the peak associated with the aTA and EA powders themselves. The samples then thermally degrade at 575°C as in the control and TA samples. aTA and EA samples did not show signs of thermal degradation at the 350°C peak, which was associated with the thermal degradation of the thermoset network. The aTA samples showed increased char yield as compared to the EA samples.

This result in thermal degradation suggested that the initiation of the thermal degradation pathway for aTA and EA samples is dependent upon the aTA and EA in the sample and not the thermal stability of the thermoset network. The degradation of the acetyl functionality in the molecule initiates thermal degradation of the composite material. This could be because the acetyl groups on the TA molecule are cleaved which are then able to initiate the thermal degradation of the thermoset network at lower temperature. However, although the decrease in mass at this temperature is significantly less than the control or just TA-containing samples, the resulting char from this process is more thermally stable resulting in increased mass of samples past the temperature of thermal degradation. The resulting char from this process to the same temperature as the char in the control samples.

This degradation pathway in compressed air could indicate that acetylated TAs could increase the flame retardancy of the system. This is evidenced by a few aspects of the thermal degradation. Firstly, the additive when acetylated initiates material degradation at a lower temperature than the control thermoset which means the response time to char formation at the initiation of a fire is quicker. As the char is the main method through which the molecule can act as a flame retardant, the quicker this is formed the faster the fire can be cut off from its fuel. Secondly, the acetylated additives cause *less of the material to degrade* in the fire thereby reducing the amount of fuel, in the form of reactive oxidative species, made available to the flame front. Thirdly, the thermal degradation of these acetylated additives results in more volume of the thermally stable char which can form a thermally stable barrier between the flame front and the bulk material. The reaction time, reduction in loss of material, and char volume could synergistically increase the flame retardancy of the overall epoxy thermoset. While response time is consistent between aTA and EA samples, results suggest that aTA samples can produce more char than EA samples on average. For this reason, it is expected that the flame retardant ability would be higher for aTA than EA samples.

4.3.4 Thermomechanical Analysis

Thermomechanical analysis of samples was performed to study how the compatibility change of the powders in the resin affected the crosslinking density and the glass transition temperature of the thermosets (Figure 4.9). Samples containing TA powder showed initial increase in the crosslinking density and storage modulus at room temperature but past the compatibility limitations the solutions were found to decrease overall. There were no significant changes to the glass transition temperatures of the thermosets regardless of TA loading level. Thermosets containing aTA powder were found to have an increase in the glass transition temperature in the 0.1 and 1% aTA samples, but no changes in the 0.32 and 3% samples. Glass transition temperature was found to also increase with aTA addition. EA samples showed a general downward trend in crosslinking density and storage modulus, with a decrease being observed in samples loaded past 0.32%. Glass transition temperature was not found to significantly change with EA addition.

Results show that the compatibility of the powders in epoxy and the thermomechanical properties trended similarly in the case of TA. Because of the limited compatibility of TA and resin, in order to minimize the surface energy of the system the molecules separate into distinct phases, ones that appear on optical microscopy as brown-ish agglomerations that are TA-, aTA- or EA-rich, and more continuous ones that are translucent and epoxy-rich. In the TA-rich phases, there is likely a very small amount of epoxy resin that is able to dissolve. Because there is expected to be very little epoxy resin in this phase, it is likely that the crosslink density is significantly lower in this phase of the material. While it is anticipated that TA could be crosslinking into the epoxy thermoset system, the apparent decrease in global material crosslink density from DMA suggests that this reaction is not able to affect the thermomechanical properties of the composite system. However, in the epoxy-rich phases, the samples have the highest, local crosslink density due to the proximity of epoxy resin and hardener. It is likely that there is TA in these epoxy-rich phases as TA does have limited compatibility in epoxy (<1 wt%). At the temperature of thermosetting, the precursor units (resin and hardener) can react and form the thermoset polymer. The increase in apparent global crosslinking density reported by the DMA suggests that these molecules are crosslinking into the network, thereby increasing the average global crosslinking density but not changing the average global glass transition temperature. Above the compatibility limit the agglomerations formed are large compared to the size of the individual TA molecule and decrease the global average crosslink density as compared to the 0.1 wt% sample. Interestingly, the presence of agglomerations did not significantly change the global crosslinking density of the TA-epoxy composites as compared to the control sample at the loading levels explored for this study. In the samples containing agglomerations, it is likely that the TA in the epoxy phase is crosslinking into the network as seen in the 0.1-1 wt% TA samples. However, this crosslinking is not enough to counteract the decrease in mechanical properties created by the TA-rich phases. These results suggest that if compatibility limitations can be circumvented the resulting material may have increased thermomechanical stability.

In the aTA samples, while 0.1 wt% samples showed a significant increase in the crosslink density and storage modulus, this result did not maintain for concentrations past this point. However, the T_g was found to increase significantly for samples in which 1 wt% or higher of the additive was loaded. The initial explanation for this behavior is that aTA, which is partially modified with acetic anhydrideacetylated, is able to crosslink into the epoxy system as suggested by previous work. However, this crosslinking density, which should be decreased as compared to TA samples, is either 1) not able to offset the decrease in crosslink density caused by the phase separation within the system at the higher loading levels and/or 2) the crosslinking density as a molecule is not significantly increased as compared to TETA, which is the case for unmodified TA. The EA samples loaded at 1wt% or higher showed a significant reduction in the crosslink density and storage modulus at room temperature, but no significant change in the T_g. This could be the result of TA being unable to crosslink into the system as it is maximally surface functionalized. The comparably large and stiff-TAacetylated TA molecules could instead occupy space in the system sterically reduceing the material's ability to crosslink, but not being comparatively stiffer not reduceits T_g. This suggests that the larger polyphenolic EA molecules get in the way of crosslinking resulting in the global average crosslinking density decreasing. This effect does not change the glass transition temperature in the EA-epoxy thermosets because the glass transition temperature is a metric of the thermal motion of the bonds in the thermoset which has not changed in these samples, though their density has changed.

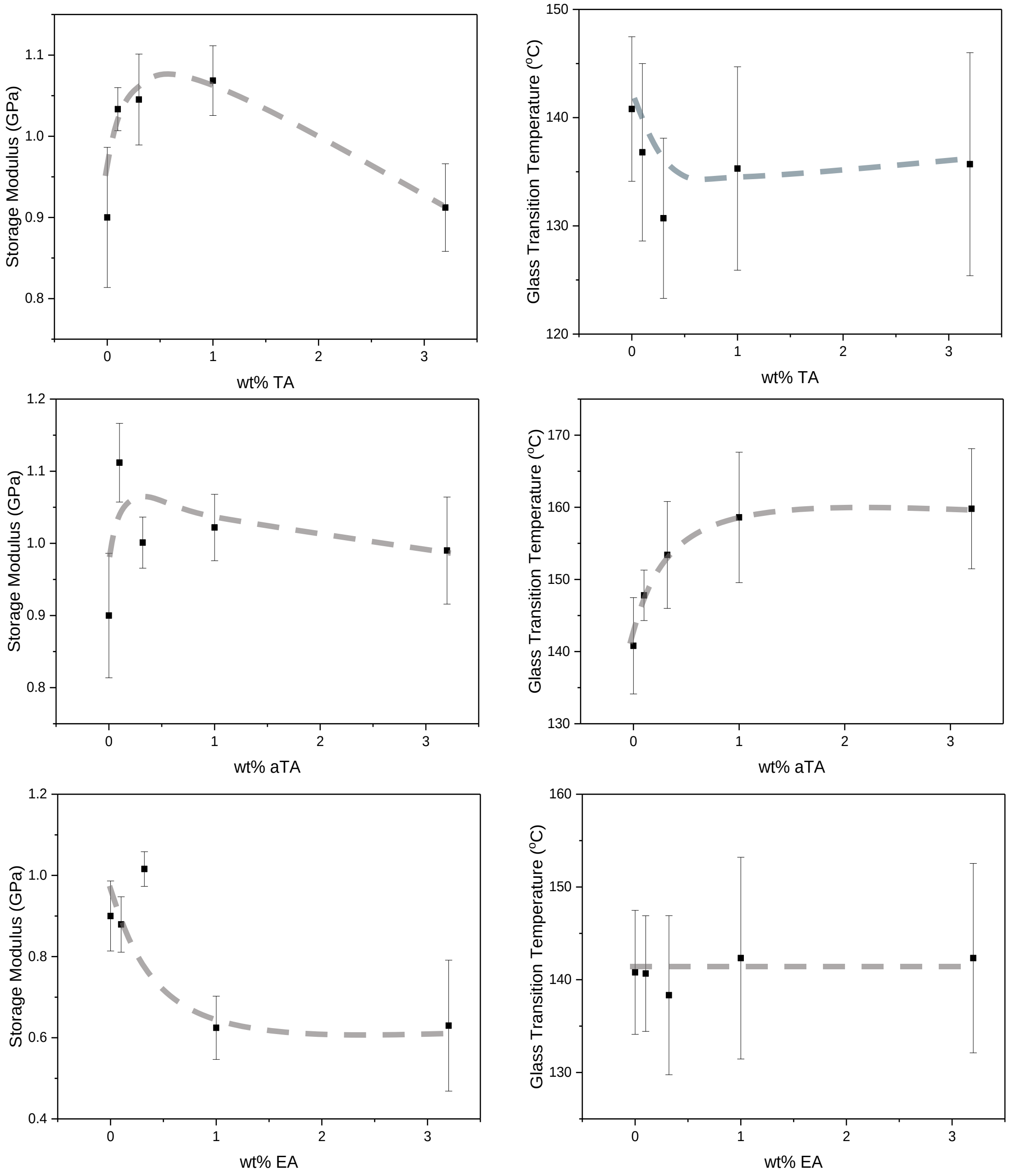


Figure 4.9: Dynamic mechanical analysis of samples. Lines were added to aid the eye.

The results of this work also indicate that chemical functionalization to increase compatibility of TA through acetylation of the molecule is a balancing act. Chemical modification increases compatibility but if done too much it can also simultaneously negatively impact the resulting mechanical properties of the thermoset. Increasing compatibility such that the molecule will dissolve in the resin, but not too much to prevent crosslinking is critical.

4.3.5 Flame Retardant Testing

Samples were then analyzed by mass loss calorimetry (MLC) to understand their behavior in a fire (Table 4.2 and Figure 2.1). Surprisingly, TA samples were not found to significantly change any of the measured properties of the material in a fire regardless of loading level. However, aTA samples were found to significantly reduce the maximum rate of heat release (RHR) in the 1 wt% and 3 wt% samples, with a nearly 80% reduction in the value at a 3 wt% loading level. Additionally, the 3 wt% aTA samples saw a significant increase to the total mass loss and the peak mass loss rate. EA samples significantly decreased the peak heat release rate, but at 3 wt% EA this trend was not followed. No samples showed significant changes to the TTI.

Table 4.2: MLC Results from Samples. Samples in bold with asterisks indicate they are significantly different form the control samples ($p<0.05$).

	Time to Ignition (s)	Total Mass Loss (g)	Peak Mass Loss Rate (g/min)	Peak Rate of Heat Release (RHR) (kW/m^2)	Total Heat Release (MJ)
Control Epoxy	91.6 ± 14.9	30.3 ± 2.6	43.6 ± 6.5	954.5 ± 111.1	86.4 ± 4.4
0.1 wt% TA	99 ± 3.7	34.3 ± 3.9	47.8 ± 4.5	1004.8 ± 34.7	93.9 ± 8.6
1 wt% TA	92 ± 11.2	33.5 ± 1.9	47.7 ± 4.1	1021.2 ± 28.4	93.3 ± 5.5
3.2 wt% TA	94.7 ± 2.4	33.9 ± 1.4	48.3 ± 2.7	1050.1 ± 12.1	99.2 ± 2.2
0.1 wt% aTA	113 ± 14.7	36.6 ± 3.7	40.9 ± 4.1	896.6 ± 107.6	125.3 ± 5.0
1 wt% aTA	82 ± 22.5	34 ± 10	35.6 ± 6.5	**511.9 ± 199.3***	72 ± 30.6
3.2 wt% aTA	82 ± 7.0	**23.6 ± 1.9***	**30.6 ± 2.3***	**199.9 ± 37.9***	**17.4 ± 1.6***
0.1 wt% EA	86.3 ± 18.3	34.9 ± 8.8	40 ± 3.0	**709.9 ± 54.9***	94.2 ± 23.4
1 wt% EA	76.3 ± 12.7	36.2 ± 4.2	40.6 ± 8.3	**666.2 ± 151.8***	95.9 ± 9.5
3 wt% EA	99.7 ± 14.4	32.3 ± 4.0	49.4 ± 6.1	943.3 ± 35.5	109.8 ± 12.9

The results from MLC indicate that aTA samples showed the most promise as a flame retardant additive. This result was suggested by TGA in compressed air, where aTA samples showed the highest concentration of char at elevated temperature. TGA indicated that aTA and EA samples could have a significantly increased sensitivity to temperature increase, but MLC did not indicate this was the case. The reason for this is that the 35kW heating of the samples in MLC responds to a temperature closer to 600°C, which was significantly above the thermal degradation temperature of TA, aTA, and EA samples. The preliminary explanation for why aTA samples have such significantly better flammability comparatively is due to the residual phenol groups after chemical modification. Leading available phenol groups which could crosslink into the epoxy network during post-cure, along with the surface modification to enhance compatibility and char yield, result in reduced molecular mobility in the epoxy resulting in an increased char yield in the epoxy. This char could act as a barrier between the epoxy and the flame front reducing the fuel to the fire. These results are consistent with the expected behavior from TGA in compressed air and thermomechanical properties from TGA.

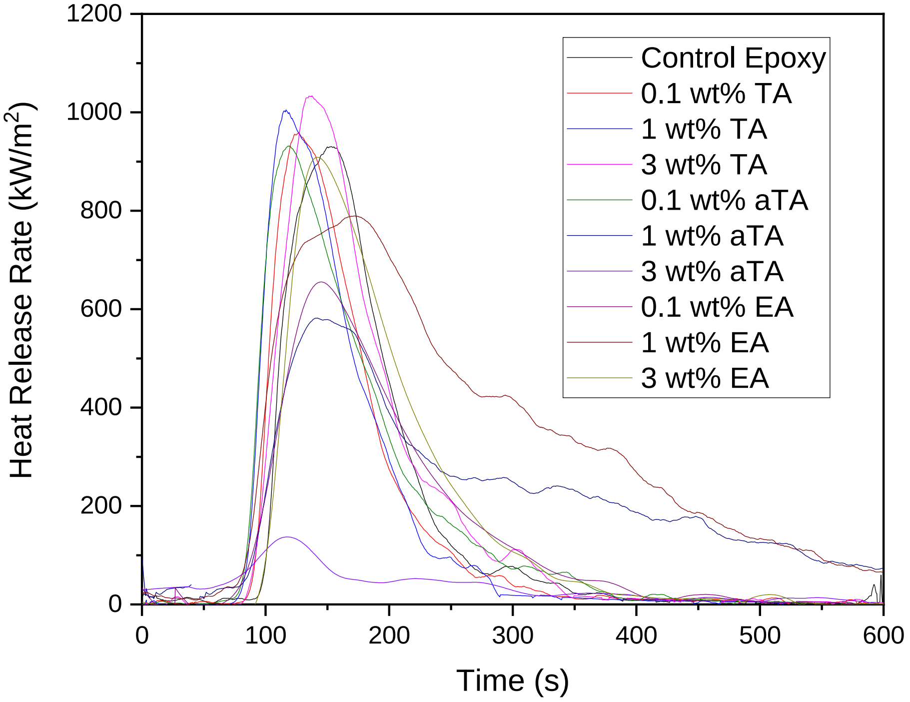


Figure 4.10: MLC of samples indicates that aTA samples showed the most significantly increased flame retardancy. Samples containing 3 wt% of aTA showed the most significant reduction.

Table 4.3: The peak RHR percent reduction for samples with significant differences from the control. 3 wt% aTA samples showed a reduction of 79% whereas TPP controls reduced the peak RHR by 43%.

Sample	Percent Reduction of Peak RHR (%)
Control Epoxy	0%
1 wt% aTA	46%
3 wt% aTA	79%
0.1 wt% EA	26%
1 wt% EA	30%
10 wt% TPP	43%

Results that had significant reductions in RHR were compared to literature values for 10 wt% of triphenyl phosphate (TPP) in epoxy using this method (Table 4.3).[14] Results indicate that the aTA samples reduce the peak RHR by 79% on average whereas the TPP controls only reduced the peak by 43%. This result suggests that aTA samples may have a better flame retardant response as compared to the TPP controls. Since TPP is available and utilized commercially, this may indicate that aTA samples could out-perform commercially available epoxy flame retardants.

4.4 Conclusions

In this work, biologically-based and non-toxic TA was acetylated to increase compatibility in epoxy and studied as an alternative flame retardant for these thermosets. The results from this work showed that the degree of acetylation of the molecule had a significant impact on the ability for the molecule to work as a flame retardant and on its thermomechanical properties. Higher acetylation of TA resulted in a reduction of the flame retardant ability at higher loading levels due to the inability for the molecule to crosslink with the thermoset. Samples that were partially acetylated showed a significant reduction in PHR, MLR, and THR which was largely attributed to the presence of residual phenol groups. The result from this work shows that through partial acetylation the flame retardancy of TA can be enhanced significantly. It is the hope of the researchers that this work could be used to decrease the environmental and health impacts of the use of epoxy thermosets around the world.

4.5 Acknowledgements

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4.6 References

1. Maley, A. M.; Falk, K. A.; Hoover, L.; Earlywine, E. B.; Seymour, M. D.; Deyoung, P. A.; Blum, A.; Stapleton, H. M.; Peaslee, G. F., Detection of halogenated flame retardants in polyurethane foam by particle induced X-ray emission. *Nuclear Inst. and Methods in Physics Research, B* **2015,** *358* (C), 21-25.
2. Stapleton, H. M.; Sharma, S.; Getzinger, G.; Ferguson, P. L.; Gabriel, M.; Webster, T. F.; Blum, A., Novel and high volume use flame retardants in US couches reflective of the 2005 PentaBDE phase out. *Environmental science & technology* **2012,** *46* (24), 13432.
3. Babrauskas, V.; Lucas, D.; Eisenberg, D.; Singla, V.; Dedeo, M.; Blum, A., Flame retardants in building insulation: a case for re-evaluating building codes. *Building Research & Information* **2012,** *40* (6), 738-755.
4. *Flame Retardants in Printed Circuit Boards*; Environmental Protection Agency: 2014.
5. Eskenazi, B.; Chevrier, J.; Rauch, S.; Kogut, K.; Harley, K.; Johnson, C.; Trujillo, C.; Sjödin, A.; Bradman, A., In Utero and Childhood Polybrominated Diphenyl Ether (PBDE) Exposures and Neurodevelopment in the CHAMACOS Study. *Environmental Health Perspectives (Online)* **2013,** *121* (2), 257.
6. Liu, Z.; Liu, D.; Cheng, J.; Mei, S.; Fu, Y.; Lai, W.; Wang, Y.; Xu, Y.; Vo, T. D.; Lynch, B. S., Lipid-soluble green tea extract: Genotoxicity and subchronic toxicity studies.(Report). *Regulatory Toxicology and Pharmacology* **2017,** *86*, 366.
7. NTP Toxicology and Carcinogenesis Studies of Decabromodiphenyl Oxide (CAS No. 1163-19-5) In F344/N Rats and B6C3F1 Mice (Feed Studies). *National Toxicology Program technical report series* **1986,** *309*, 1.
8. Darnerud, P. O.; Aune, M.; Larsson, L.; Lignell, S.; Mutshatshi, T.; Okonkwo, J.; Botha, B.; Agyei, N., Levels of brominated flame retardants and other pesistent organic pollutants in breast milk samples from Limpopo province, South Africa. *Science of the Total Environment* **2011,** *409* (19), 4048-4053.
9. Strong growth forecast for non-halogenated flame retardants. *Additives for Polymers* **2014,** *2014* (11), 11-11.
10. Waaijers, S. L.; Kong, D.; Hendriks, H. S.; De Wit, C. A.; Cousins, I. T.; Westerink, R. H. S.; Leonards, P. E. G.; Kraak, M. H. S.; Admiraal, W.; De Voogt, P.; Parsons, J. R., Persistence, bioaccumulation, and toxicity of halogen-free flame retardants. *Reviews of Environmental Contamination and Toxicology* **2013,** *222*, 1-71.

11. Han, Y.; Zhang, X.; Wu, X.; Lu, C., Flame Retardant, Heat Insulating Cellulose Aerogels from Waste Cotton Fabrics by in Situ Formation of Magnesium Hydroxide Nanoparticles in Cellulose Gel Nanostructures. *ACS Sustainable Chemistry and Engineering* **2015,** *3* (8), 1853-1859.

12. Isarov, S. A.; Lee, P. W.; Towslee, J. H.; Hoffman, K. M.; Davis, R. D.; Maia, J. M.; Pokorski, J. K., DNA as a flame retardant additive for low-density polyethylene. *Polymer* **2016,** *97*, 504-514.

13. Alongi, J.; Carletto, R. A.; Di Blasio, A.; Carosio, F.; Bosco, F.; Malucelli, G., DNA: a novel, green, natural flame retardant and suppressant for cotton. *J. Mater. Chem. A* **2013,** *1* (15), 4779-4785.

14. Mendis, G.; Weiss, S.; Korey, M.; Boardman, C.; Dietenberger, M.; Youngblood, J.; Howarter, J., Phosphorylated Lignin as a Halogen-Free Flame Retardant Additive for Epoxy Composites. *Green Materials* **2016,** *4* (4).

15. Jaime-Anne, E.; Warren, J. G.; Cole, L.; James, H. B., Esterification of Condensed Tannins and Their Impact on the Properties of Poly(Lactic Acid). *Polymers* **2013,** *5* (2), 344-360.

16. Grigsby, W. J.; Kadla, J. F., Evaluating Poly(lactic acid) Fiber Reinforcement with Modified Tannins. *Macromolecular Materials and Engineering* **2014,** *299* (3), 368-378.

17. Celzard, A.; Fierro, V.; Amaral-Labat, G.; Pizzi, A.; Torero, J., Flammability assessment of tannin-based cellular materials. *Polymer Degradation and Stability* **2011,** *96* (4), 477-482.

18. Thébault, M.; Pizzi, A.; Essawy, H. A.; Barhoum, A.; Van Assche, G., Isocyanate free condensed tannin-based polyurethanes. *European Polymer Journal* **2015,** *67* (C), 513-526.

19. Xia, Z.; Singh, A.; Kiratitanavit, W.; Mosurkal, R.; Kumar, J.; Nagarajan, R., Unraveling the mechanism of thermal and thermo-oxidative degradation of tannic acid. *Thermochimica Acta* **2015,** *605*, 77--85.

20. Garcia de Rodriguez, N. L.; Thielemans, W.; Dufresne, A., Sisal cellulose whiskers reinforced polyvinyl acetate nanocomposites. *Cellulose* **2006,** *13* (3), 261-270.

21. Roohani, M.; Habibi, Y.; Belgacem, N. M.; Ebrahim, G.; Karimi, A. N.; Dufresne, A., Cellulose whiskers reinforced polyvinyl alcohol copolymers nanocomposites. *European Polymer Journal* **2008,** *44* (8), 2489-2498.

22. Iwatake, A.; Nogi, M.; Yano, H., Cellulose nanofiber-reinforced polylactic acid. *Composites Science and Technology* **2008,** *68* (9), 2103-2106.

23. Zhong, T.; Oporto, G.; Peng, Y.; Xie, X.; Gardner, D., Drying cellulose-based materials containing copper nanoparticles. *Cellulose* **2015,** *22* (4), 2665-2681.

24. Barari, B.; Ellingham, T. K.; Qamhia, I.; Pillai, K. M.; El-Hajjar, R.; Turng, L.-S.; Sabo, R., Mechanical characterization of scalable cellulose nano-fiber based composites made using liquid composite molding process. *Composites Part B* **2016,** *84* (C), 277-284.

25. Peng, S. X.; Shrestha, S.; Yoo, Y.; Youngblood, J. P., Enhanced dispersion and properties of a two-component epoxy nanocomposite using surface modified cellulose nanocrystals. *Polymer* **2017,** *112*, 359-368.

26. Society of Plastics, E., *Tannic Acid: A Bio-Based Intumescent Char-Forming Additive for Nylon 6*. Society of Plastics Engineers: 2016; p 1-5.

27. Burkinshaw, S. M.; Bahojb-Allafan, B., The development of a metal-free, tannic acid-based aftertreatment for nylon 6,6 dyed with acid dyes. Part 4: tannic acid. *Dyes and Pigments* **2004,** *62* (2), 159-172.

28. Ontiveros-Ortega, A.; Espinosa-Jiménez, M.; Chibowski, E.; González-Caballero, F., Effect of Tannic Acid on the Surface Free Energy of Polyester Dyed with a Cationic Dye. *Journal of Colloid And Interface Science* **1998,** *199* (1), 99-104.

29. Ge, J.; Shi, X.; Cai, M.; Wu, R.; Wang, M., A novel biodegradable antimicrobial PU foam from wattle tannin. *Journal of Applied Polymer Science* **2003,** *90* (10), 2756-2763.

30. Korey, M.; Johnson, A.; Webb, W.; Howarter, J. A., *Minerals, Metals and Materials Series*. Springer International Publishing: 2019; p 83-88.

31. Korey, M.; Youngblood, J.; Howarter, J., Tannic acid: A novel intumescent agent in epoxy systems. *Abstr. Pap. Am. Chem. Soc.* **2019,** *257*.

32. Korey, M.; Mendis, G. P.; Youngblood, J. P.; Howarter, J. A., Tannic acid: A sustainable crosslinking agent for high glass transition epoxy materials. *Journal of Polymer Science Part A: Polymer Chemistry* **2018,** *56* (13), 1468-1480.

5. TANNIC ACID – A SUSTAINABLY-SOURCED REACTIVE EPOXY THINNING AGENT

This work is currently accepted for submission to the *International Conference on Flame Retardant Plastics* in Athens, Greece (2020). This chapter is based off work performed in collaboration with Sam McClellan, a high school teacher who was part of a summer RET program with me. For this work, Sam performed the solvent testing in MEK and took the optical microscopy pictures. However, the writing and analysis for this work was done by me along with mentorship and intellectual input from my advisors.

5.1 Abstract

Background & Significance: Tannic acid (TA) is a bio-based high molecular weight organic, aromatic molecule that has been found to increase thermal stability and flame retardancy of many polymer matrices when used as an additive. Although it is biologically sourced, TA is a pollutant in industrial wastewater streams, and there is desire to find applications in which to downcycle this molecule after extraction from these streams. Additionally, epoxy thermosets have revolutionized many industries, but are too flammable to be used in many applications without additives which augment their flame retardancy (FR). Many flame retardants used in epoxy thermosets are synthesized from petroleum-based monomers leading to significant environmental impacts at the industrial scale. Many of these compounds also have significant impacts on human health. Various bio-based modifiers have been developed to improve the FR of the epoxy resin; however, increasing FR of the system without tradeoffs with other properties has proven challenging. **Methodologies:** In this work, TA was incorporated into the thermoset by use of solvent-exchange using methylethyl ketone, a co-solvent for TA and epoxy resin. Samples were then characterized optically (UV-vis spectroscopy and optical microscopy), thermally (thermogravimetric analysis and differential scanning calorimetry), and for their flame retardancy (mass loss calorimetry). **Major Findings:** Compared to control samples, all samples were found to have increased thermal stability. Further, the addition of tannic acid to the polymer matrix by use of solvent greatly increased the compatibility of the additive in epoxy thermosets. By using solvent-exchange the highest loading level of TA found in literature was achieved in this work (40 wt%).

5.2 Introduction

In 2015 global plastics demand exceeded 300 million tons, and this value is growing steadily.[1, 2] Since 1980, the plastics industry has grown at an annual, average rate of 3.4 percent, with US plastics companies alone employing over 1 million workers and providing nearly $379 billion in annual shipments.[1, 2] Plastics (or polymers) are used in a variety of applications due to their low density, the ease with which they are processed, and low cost.[3] Polymers can be designed to have properties desirable to a multitude of applications. Thermoplastic polymers, such as nylon, polyethylene, or polyvinyl chloride, are found in applications such as piping, food packaging, insulation, and clothing.[4] Thermoset polymers, such as epoxies and polyurethanes, are often found in coatings, structural applications, and adhesives.[5-7] Though these materials are often lower in cost to many materials previously utilized, there are challenges that still face their adoption into application – especially for epoxy.

An epoxy thermoset is often made of two constituent chemicals: an epoxy resin and a hardening agent, which react to form a molecular-level, dense, covalent chemical network. Epoxies are desirable for many applications due to their low cost, their excellent mechanical strength, good thermal, electrical, and chemical resistance and superb adhesion to many substrates. For this reason, they are used in a wide range of applications including coatings,3 adhesives,4 structural composites,5 insulating materials,6 and in components of electronics.7,8 Global epoxy market demand is expected to increase at a compound annual growth rate of 7.9% from 2016 to 2020, with an expected annual demand of 2,115.6 ktons in the coatings sector alone by 2024.9-11 However, though epoxy has innate properties that are desirable there are additional challenges with its use in many applications. For this reason, during processing many additional additives are put into the system including including toughening agents – which make the epoxy less brittle upon failure, chemical accelerants – which enable the crosslinking to happen more quickly or at lower temperature, flame retardants – which enhance the innate flame retardancy of epoxies , and thinning agents – which reduce the viscosity of epoxy resin – just to name a few.

While epoxy exhibits high mechanical resistance and durability, its low workability and high viscosity is a challenge in many applications including construction.[8] To circumvent this, many solutions have been developed. One such solution is the use of thinning agents of which there are two types: reactive and unreactive. Reactive thinning agents are molecules containing one or more functional groups that decrease viscosity while participating in crosslinking reaction while non-reactive thinning agents are typically organic solvents that decrease viscosity but are used in less than 10 wt% of the pre-polymer so as to not affect the quality of the final product.[8, 9] However, each of these methods has benefits and proposes unique challenges, especially non-reactive. The use of non-reactive thinning agents has declined because of the reduction of mechanical properties that usually accompanies their use. The use of small amounts of non-reactive thinning agents can reduce epoxy's compressive strength by 35%, extend curing time, cause epoxy to shrink and crack over time, and damage some substrates.[10] For this reason, many will thin epoxy using heat alone which can result in epoxy curing too quickly and causing poor material performance.[8, 10]

Tannic acid (TA) is a bio-based high molecular weight organic, aromatic molecule that has been found to increase thermal stability, thermomechanical properties, and flame retardancy of many polymer matrices when used as an additive.[11-17] Although it is biologically sourced, TA is a pollutant in industrial wastewater streams, and there is desire to find applications in which to downcycle this molecule after extraction from these streams.[18-22] Previous research has shown that TA reacts with epoxy resin at elevated temperature resulting in highly crosslinked, tough, and hard epoxy materials.[17] However, these TA-DGEBA mixtures are extremely viscous at room temperature and not workable.[17] TA is also soluble in non-reactive thinning agents used for epoxy, such as methyl ethyl ketone (MEK).[23] Because TA reacts at elevated temperature, mixing MEK, resin, and TA could potentially create a 1-part epoxy thermoset which could be applied at room temperature with low viscosity and then dried at elevated temperature.

The use of TA as a method of enhancing MEK-thinned epoxy, and additionally potentially affecting the flame retardancy of the system, has not been previously explored in the literature. The hope of this work was to develop a novel thinning agent system with non-reactive (MEK) and reactive (TA) functionality. In this work, the dispersion of TA into epoxy systems using non-reactive epoxy thinning agent – methylethyl ketone (MEK) – will be explored. The result of this work indicated that the use of solvent can decrease the temperature of reaction of TA and DGEBA from 175°C to as low as 80°C resulting in a thermoset system that in its pre-polymer phase has low viscosity and can be hardened without the need for additional hardening agent.

5.3 Methods

5.3.1 Materials

TA, triethylene tetramine (TETA) and MEK were purchased from Sigma Aldrich (St. Louis, MO, USA). EPON 825 (DGEBA) resin was purchased from Hexion, Inc. (Louisville, KY, USA). Mold Max 60 silicone precursor and initiator – parts A and B - were purchased from Smooth-On, Inc. (Macungie, PA, USA). 20mL borosilicate scintillation vials were purchased from Thermo Fisher Scientific (Waltham, MA, USA).

5.3.2 Preparation of TA-MEK-DGEBA composites

TA and MEK were mixed varying weight percentages (0-75 wt% TA) at 1250 rpm for 3 minutes using a Flacktek speedmixer (SpeedMixer, Landrum, SC, USA).

A catalogue of TA samples were studied in epoxy. Two distinct samples sets were prepared. Initially, samples were prepared as done in industry with MEK being dispersed into epoxy and hardened using TETA at room temperature overnight (Table 5.1). As can be seen in the table, sample 0 is a control sample without any MEK added. Samples 1 and 2 are MEK control samples at 5 and 10 wt% respectively. Samples 3 and 4 are samples with the MEK wt% consistent with the control samples with added TA on top of the MEK. Note that the wt% of the thinning agent in this case (32% TA in MEK) is higher than in the control samples, but the wt% of solvent is consistent. Sampels 5 and 6 have consistent thinning agent (32% TA in MEK) as compared to the control sampels, but these samples contain less of the solvent than the control samples. These samples were dried overnight at room temperature and then analysed, as done in industry. Mechanical testing samples were prepared by pouring epoxy samples into a 10mL syringe and drying overnight. Samples were removed from the plastic syringe and polished to ensure parallel top and bottoms to samples.

Table 5.1: Solutions prepared using TA, MEK, DGEBA, and TETA hardener.

Sample Label	TA %	MEK %	MEK and TA %	DGEBA %	TETA %
0	---	0%	0%	85%	15%
1	---	5%	**5%**	81%	14%
2	---	10%	**10%**	77%	13%
3	1.6%	3.4%	**5%**	81%	14%
4	3.2%	6.8%	**10%**	77%	13%

Considering that TA has been found to crosslink epoxy in the literature, and a 32% TA could be achieved in MEK, a second set of samples were prepared by mixing the dispersions into the DGEBA without hardener. These percentages were used because with the removal of 100% of solvent one would obtain the final weight % of TA up to 40% (Table 5.2). Samples in this case were prepared as above but then dried using a rotovap for 4 hours and a vacuum oven at 80°C for 6 hours as the highly TA-loaded samples contained a very significant amount of solvent that needed to be removed.

Table 5.2: Solutions Prepared using TA as the hardener.

Sample Label	Final Theoretical Weight % TA	TA % Before Dry	MEK % Before Dry	DGEBA % Before Dry
5	5%	5%	10%	86%
6	10%	8%	18%	74%
7	25%	16%	35%	49%
8	40%	22%	46%	32%

5.3.3 Sample Characterization

Optical Microscopy was performed using a Zeiss optical microscope (Zeiss, Thornwood, NY, USA). Samples were prepared by pouring 5 mL of sample onto a microscope slide. Spacers were used on either side of the sample to ensure consistent sample thickness and a microscope slide was placed on top. Image analysis was done using ImageJ (National Institute of Health, Bethesda, MD, USA).

Attenuated total reflectance (ATR) Fourier transform infrared (FTIR) spectroscopy was performed using a PerkinElmer Spectrum 100 FTIR Spectrometer (PerkinElmer, Seer Green, Beaconsfield, UK) outfitted using a zinc selenide (ZnSe) crystal. Samples were scanned from 650 cm$_{-1}$ to 4000 cm$_{-1}$ in transmissive model. Epoxy samples of thickness 0.35 cm containing the powders as additives at 0.32 wt% and peaks were normalized to a control epoxy sample. These samples were not cured as above but were instead set at room temperature to avoid reaction between TA and epoxy resin. Samples were scanned 4 times and normalized to the phenyl peak at 1605 cm$_{-1}$ using Spectra (PerkinElmer, Seer Green, Beaconsfield, UK). 3 samples were analyzed for each powder. Absorbance values were calculated using Spectra (PerkinElmer, Seer Green, Beaconsfield, UK) and were averaged between samples.

Thermogravimetric analysis (TGA) was performed with a Q50 thermogravimetric analyzer (TA Instruments, Newcastle, DE, USA). Samples were prepared for TGA analysis by shaving off sample from epoxy products. Experiments were performed in nitrogen with a 60 mL/min flow rate using a 15 °C/min heating rate from 30 °C to 900 °C. Three epoxy samples were run at each concentration and results were averaged. T_d was determined by finding the peak of the mass loss rate curve using Universal Analysis (TA Instruments, Newcastle, DE, USA) and averaging the temperature values at this point.

Differential Scanning Calorimetry (DSC) was performed on liquid pre-polymer samples using a Q2000 Differential Scanning Calorimeter (TA Instruments, Newcastle, DE, USA). Samples were loaded into aluminum pans and run using a heat/cool/heat cycle from –50 °C to 250°C with a heating and cooling rate of 10 °C/min. Three samples were run at each concentration and the mean glass transition value of the second heat curve was calculated as the midpoint of the incline observed on thermograms and averaged for each concentration using Universal Analysis (TA Instruments, Newcastle, DE, USA).

Statistical analysis was performed using JMP (SAS Institute, Cary, NC, USA). A student's t-test was run to compare samples. A p-value <0.05 was used to indicate statistically significant differences between samples. Regression analysis was performed using OriginPro 2017 (OriginLab Inc., Northampton, MA, USA). Results were fit to an exponential decay and linear models, and the reported equations and standard error (S_e) values were output by the software after regression analysis. S_e values <0.05 were determined as appropriate fits for the regression.

Mechanical testing was performed using a compression fixture on a Mechanical testing frame (MTS Instruments, Eden Prairie, MN, USA). Cylindrical samples were prepared with dimensions of 14.81 ± 0.03 and 21.15 ± 1.6 mm as the diameter and height respectively. 2 samples were run at each concentration and they were loaded to break, which was determined by observable cracking and fracture on the surface of the part. Toughness values were obtained by integrating the stress/strain curves using OriginPro 2017 (OriginLab Inc., Northampton, MA, USA).

5.4 Results & Discussion

MEK was utilized to aid the dispersion of TA into epoxy resin. In order to obtain the most concentrated TA/MEK solution that could still be mixed into the resin, a catalogue of TA-MEK concentrations were studied (Figure 5.1). TA was visually found to disperse at all concentrations up to 50 wt%. However, at concentrations at or above 50 wt% TA, the solutions were too viscous to mix using a magnetic stir bar on a stir plate. For this reason, the 32 wt% TA solution was determined as the maximum concentration of TA in MEK that could still thin the epoxy resin. It was pursued for this study moving forward.

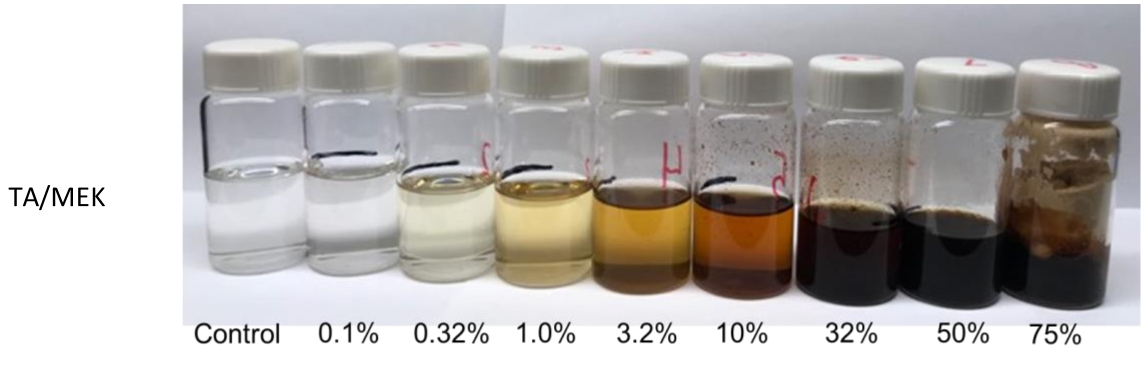


Figure 5.1: A visualization of the samples of TA in MEK from 0-75 wt%.

5.4.1 Dispersion of TA into DGEBA using MEK

Samples of 5 and 10 wt% of 0% and 32% TA in MEK were hardened with TETA. Samples were analysed using TGA to understand thermal properties (Figure 5.2).

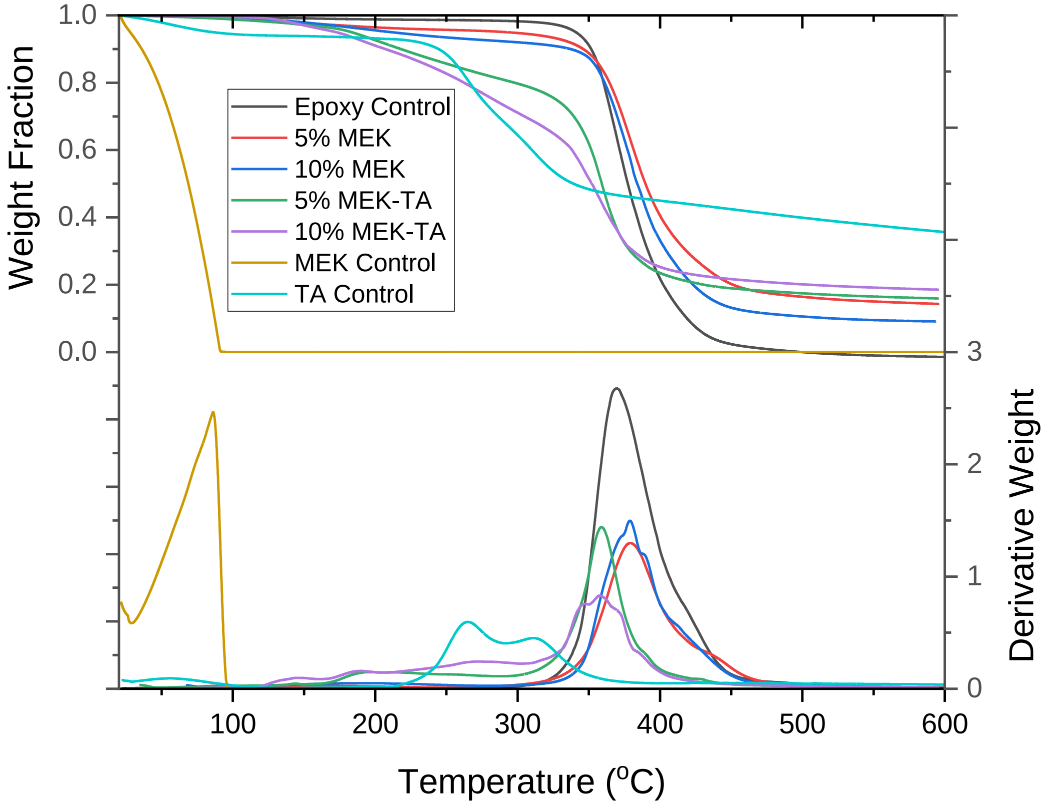


Figure 5.2: Thermal degradation of thinned epoxy samples using MEK and TA compared to control samples. As can be seen, addition of thinning agent and TA changed thermal degradation pathways.

Thermal degradation was significantly changed between samples. As can be seen, MEK boils off at temperatures below 100°C. Control epoxy samples thermally degraded at 380°C and degraded to 0% weight indicating little to no char remained at completion of the test. The 5 and 10% MEK and MEK-TA samples showed an initial thermal degradation at around 150°C, which was likely residual MEK in the samples. This residual MEK is perhaps not readily available to degrade at room temperature because it is likely solvating DGEBA and TETA in the samples. MEK samples also showed a reduction of the magnitude of the derivative weightand char remaining at completion of the test as compared to control. The 10% solvent samples had a reduced amount of remaining char at completion of the test as compared to the 5% sample. The addition of TA surprisingly reduced the temperature of thermal degradation of the samples in both cases as compared to the MEK controls. Both the 5 and 10% MEK-TA samples had an increased char remaining at completion of the test as compared to 5 and 10% MEK samples.

TGA results indicate that all samples likely contained residual MEK after 7 days of curing at room temperature, and unsurprisingly the amount of remaining MEK in samples was dependent on the amount of MEK added at the start (i.e. 10% had more remaining than 5%). The 5 and 10% MEK-TA samples showed that there was additionally unreacted TA in the samples that was able to thermally degrade at or near the thermal degradation temperature of TA. No significant change was found in the temperature of thermal degradation of any of the epoxy samples, regardless of whether or not they were thinned as compared to the control. However, the amount of char at competion of the test was significantly increased in all samples containing MEK. This could be because as MEK degrades in the epoxy some of it is able to react into the network.enabling a more thermally stable char to form. It is unsurprising that samples containing TA would have higher char yields as control TA degradation results in a thermally stable char.

Samples were analysed by DSC to further understand how residual thinning agent and TA affected the thermomechanical properties (Figure 5.3).

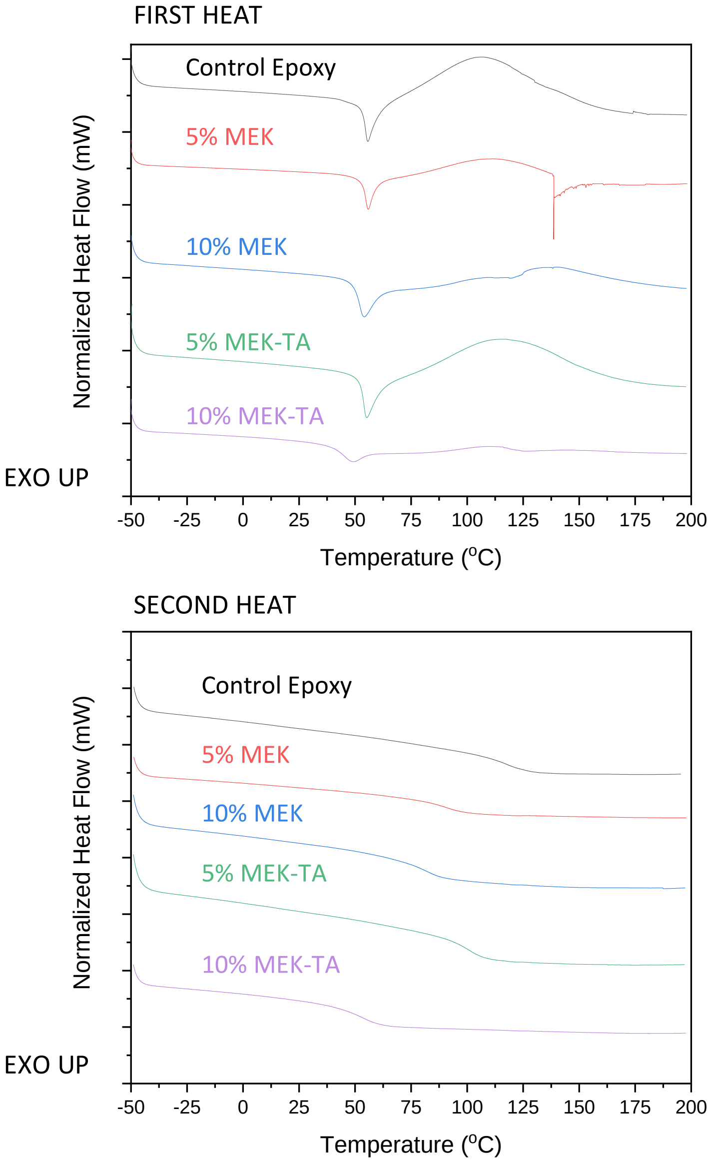


Figure 5.3: Solvent-dispersed samples were analyzed via DSC. The top picture is the result during the first heat, and the bottom figure is the result during the second heat.

DSC thermograms indicated that after setting, samples showed an endothermic transition around 50°C, which is likely the result of unreacted DGEBA in solution. This After that point, samples show a large exothermic curve, which is likely the samples curing. As indicated by the first heat curve, all samples had evidence of undercure which was unsurprising. The second heat curve showed the resulting glass transition of this cure, and the values were specified further (Table 5.3). Control epoxy samples had the highest Tgs and as more MEK was added to the system the Tg decreased. The decrease observed visually in DSC was not found to be significant for 5% samples in either case; however, 10% samples in both cases were found to have significant ($p<0.05$) reductions as compared to control.

Samples were then dried for 7 days to match procedure in industry and the mechanical properties of samples were additionally characterized (Table 5.3 and Figure 5.4).

Table 5.3: Compiled Mechanical and Thermomechanical Results for TETA-hardened samples.

Sample	Glass Transition (°C)	Compression Modulus (MPa)	Ultimate Strength (MPa)	Fracture Toughness (MJ/m³)	Strain at Break (mm/mm)	Shore D Hardness
Control Epoxy	116.2 ± 9.1	31.6 ± 6.47	1.61 ± 0.31	0.41 ± 0.09	0.06 ± 0.009	47.9 ± 3.0
5% MEK	88.7 ± 9.1	42.7 ± 7.3	6.81 ± 0.19	10.85 ± 1.23	0.27 ± 0.014	49.6 ± 3.0
10% MEK	80.7 ± 9.8	34.5 ± 1.3	5.19 ± 0.10	7.07 ± 0.45	0.21 ± 0.013	43.1 ± 2.5
5% MEK-TA	99.4 ± 8.7	38.2 ± 0.78	4.65 ± 1.22	5.64 ± 1.4	0.22 ± 0.003	50.6 ± 4.7
10% MEK-TA	53.3 ± 8.6	29.3 ± 1.2	5.07 ± 0.06	7.65 ± 0.46	0.25 ± 0.004	51.0 ± 3.2

Results showed that control epoxy samples all experienced brittle failure with very little plastic deformation. All samples containing MEK and the 32% TA-MEK solutions showed significantly increased ultimate strength, fracture toughness, and strain at break. No significant changes in hardness were observed in any sample regardless of loading. Surpringly, all samples containing TA had decreased properties as compared to the MEK only control samples. These results could indicate that after 7 days of drying there was residual MEK remaining in the samples. The presence of MEK and TA in these solutions in this case would plasticize the matrix resulting in less crosslink density and more ability for molecular motion. This could explain the increase in toughness and resulting mechanical properties, as less crosslinking density should make the bulk material less brittle.

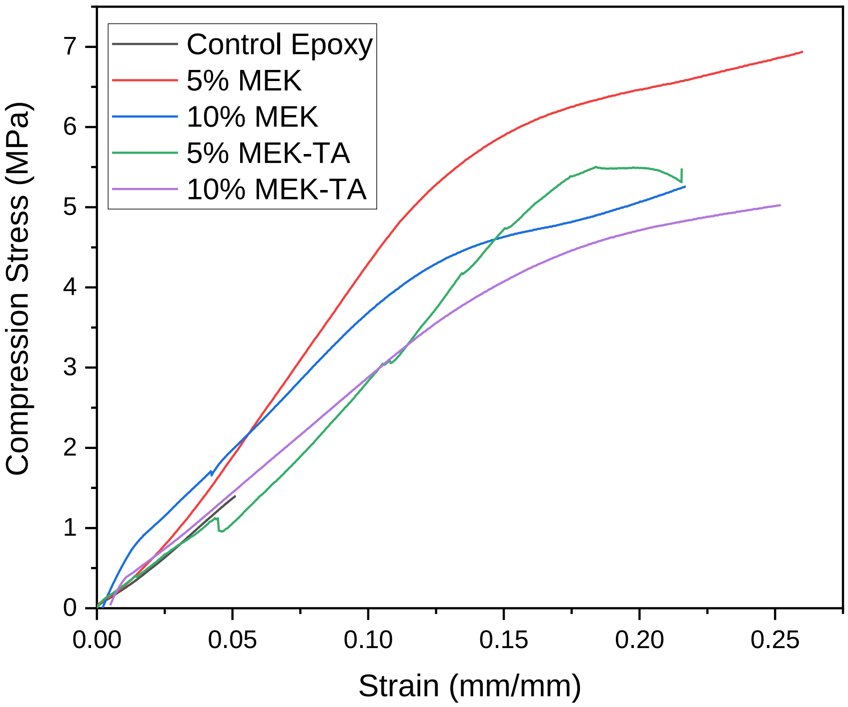


Figure 5.4: Mechanical properties of TETA-hardened, MEK-thinned epoxy samples with and without TA.

The results from this portion of the work show that dispersion of TA into epoxy using MEK and hardening with TETA does not show promise if it is dispersed as performed in industry. Residual, unavoidable MEK in the samples results in significant alterations to thermal stability, thermomechanical properties, and mechanical properties. Additionally, because TA and TETA could be reacting in the samples altering the mechanical properties of the composites, avoiding the use of TETA for this application could prove valuable. Considering TA is a biologically-sourced hardening agent,[17] there is a possibility the use of MEK could potentially enable higher loading levels of TA and lower the reaction temperature resulting in a 1 part epoxy that is thin enough to be poured. Avoiding TETA could potentially help alleviate these problems, though it would require a higher curing temperature to ensure crosslinking.

5.4.2 Dispersion of TA into DGEBA using MEK without TETA

In order to explore this, another preparation procedure was performed. The 32 wt% TA sample was dispersed into epoxy resin and concentrated using the rotavap and then a vacuum oven. The maximum concentration of TA that could be achieved using this procedure was found to be 40 wt% TA in epoxy. After solvent was removed, samples were found to be significantly more viscous, and in the case of 10 wt% TA or higher, too viscous to pour out of containers.

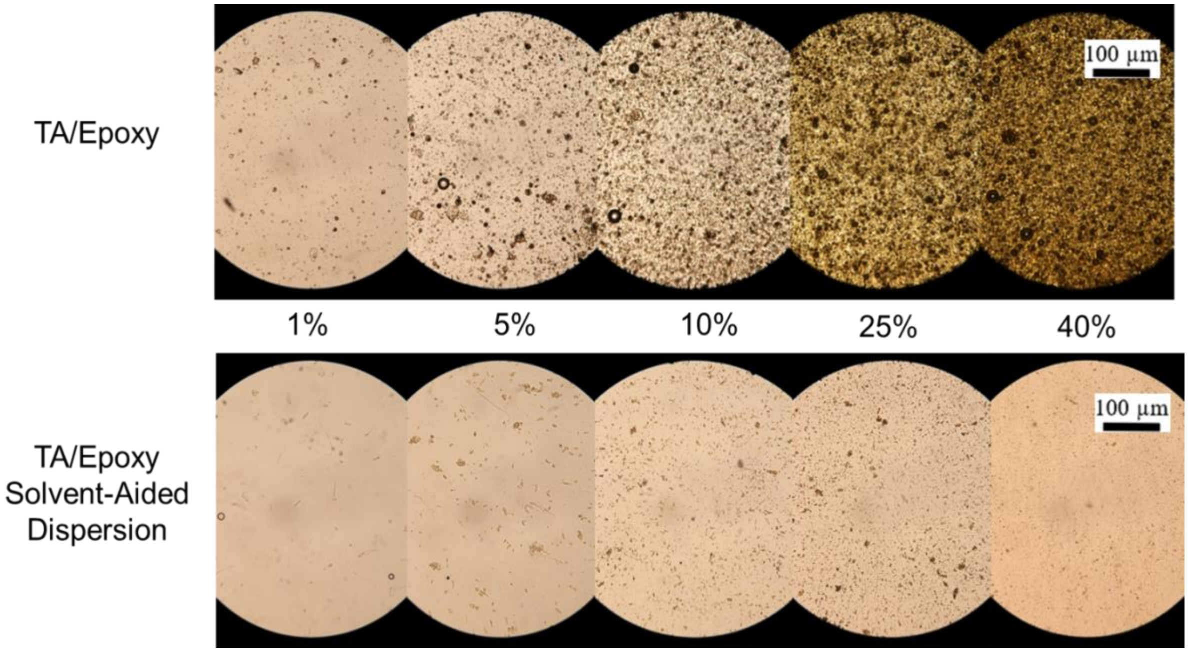


Figure 5.5: TA dispersed with (bottom) and without (top) solvent as observed via optical microscopy.

Samples were analyzed using optical microscopy (Figure 5.5). A marked visual difference in compatibility was found between TA-epoxy samples and TA-MEK-epoxy samples. Samples dispersed without solvent show a significant decrease in compatibility as TA was loaded into the samples. TA-MEK samples did not show any significant change in compatibility in any samples, though a visual increase in tanning of the samples can be observed. The results from this portion of the work show better compatibility and higher loading levels of TA into epoxy than any previous work in this area.[17]

Samples were additionally studied via UV-vis spectroscopy to better visualize the differences in compatibility (Figure 5.6). Samples of TA dispersed in epoxy resin without solvent were found to decrease to near 0% transmittance with the addition of only 0.3 wt% TA. All samples loaded above this concentration were found to have 0% transmittance, meaning 100% of the light was absorbed, scattered, or reflected by the sample and resulted in a visibly opaque sample. The use of MEK to disperse the TA showed a marked significant increase in compatibility. All transmittance values were significantly increased after the use of solvent-exchange with a decrease only to near 60%. This resulted in a still translucent sample even at 40 wt% TA, further supported by the optical microscopy results above.

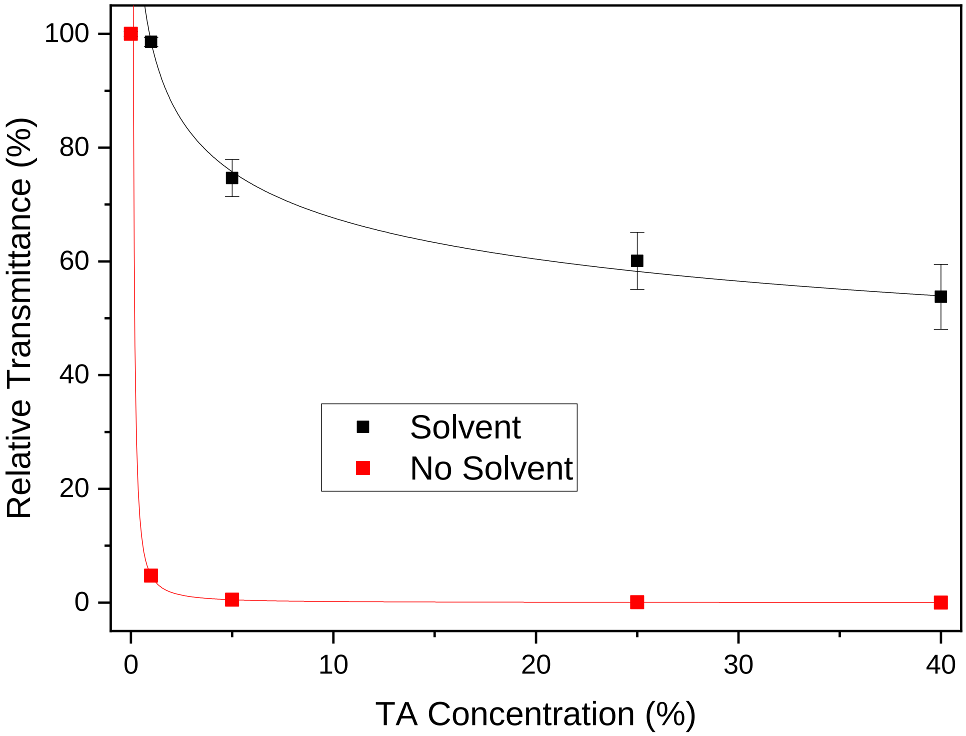


Figure 5.6: UV-Vis analysis of TA-DGEBA samples dispersed with MEK and without MEK.

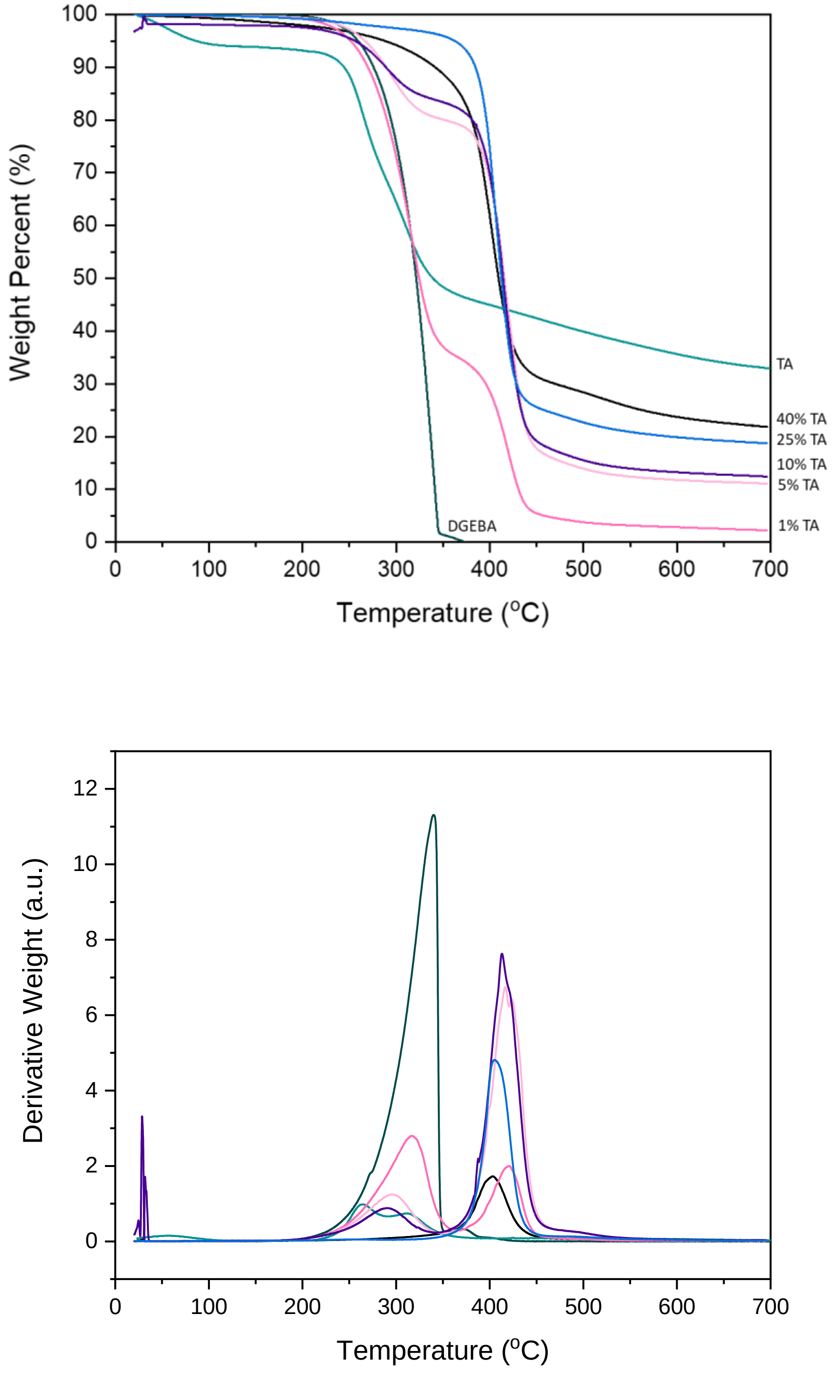


Figure 5.7: TGA of MEK-dispersed TA in epoxy.

Samples were analyzed using TGA (Figure 5.7). Results indicated that the addition of TA to epoxy significantly decreased the magnitude of the derivative weight curve for the degradation temperature at 300°C, which has been found to be associated with the degradation of epoxy resin in previous literature. Samples containing 5 and 10% TA showed degradation at the lower temperature but an additional thermal degradation at higher temperature. The rest of the samples showed a degradation peak at 400°C with an increase in magnitude which scaled with the addition of TA to the samples. This degradation temperature is consistent with previous literature which showed that degradation at this temperature was associated with TA and DGEBA crosslinking, though that reaction has only been seen in literature at higher temperature. Samples containing 25 and 40% TA showed an additional knock on the derivative weight curves at higher temperature (500°C). These results suggest that the drying procedure used in this study resulted in a ring opening reaction between TA and epoxy resin as indicated in previous literature at higher temperature (105°C). The results suggest that the use of MEK as a solvent for this reaction resulted in a decreased temperature of reaction.

In order to verify this, samples were analysed on DSC. Samples were not found to have melting temperatures associated with unreacted epoxy resin, but were found to have T_gs (Table 5.4). The T_gs were found to be dependent on TA concentration added. No significant change was observed in the T_g of 5% TA and control epoxy samples. An increase was observed between all other samples and the control. Samples loaded at 10% TA showed an elevated Tg ,but was lower than 25% TA. Samples containing 40% TA had a decreased Tg as compared to 25% samples. This result indicated that the additional solvent required to disperse 40% TA resulted in less thermomechanical stability. 25% TA samples showed the highest Tg of any sample at 102°C. These results further suggest that TA and epoxy were crosslinking at low temperature (80°C) resulting in a disappearance of the epoxy resin melting peak and resulting in a glass transition temperature associated with the crosslinked epoxy. However, they additionally show the limitation of using MEK to disperse TA into epoxy, which is the MEK can decrease thermomechanical stability.

Table 5.4: Glass transition temperature and hardness results for TA-hardened epoxy samples.

Weight Percent TA	Glass Transition Temperature (°C)	Shore D Hardness
0	-20.0 ± 1.5	---
5	-20.6 ± 3.6	---
10	38.3 ± 12.4	12 ± 0.86
25	106.3 ± 12.2	84.5 ± 2.51
40	60.1 ± 9.9	55.9 ± 2.17

The hardness of samples was measured (Table 5.4). Samples containing 5 wt% TA were a viscous liquid at room temperature. However, samples containing 10 wt% TA were a stiff gel as evidenced by the hardness value. Samples of 25% or higher TA were a very hard polymer system that was solid to the touch. These results further indicate that crosslinking was taking place in samples containing TA and DGEBA dried in this study. There was a decrease in the hardness of the 40% TA samples as compared to the 25% TA samples, which was consistent with results seen so far.

These results indicate that 25 TA is the concentration at which maximum hardness and thermomechanical properties can be achieved. This is likely the result of that concentration being closest to the 1:1 molar ratio of galloyl:epoxy (28.6 wt% TA).

5.5 Ongoing Work

Ongoing work on this project is in preparation of samples that are TA-hardened to be mechanically tested to failure. From this, the compression modulus and toughness will be obtained which will help see how these properties are affected by the use of solvent. FR samples are being prepared to be tested by either collaborators or the investigators to obtain the heat release rate.

5.6 Conclusions

Results from this work indicate that while TA may seem like a functional epoxy thinning agent additive, when utilized with TETA hardener and dried at room temperature TA does not increase the mechanical properties of the system. This shows limitation in use in the application in which aminated hardeners are utilized and samples are dried at room temperature for 7 days. However, when only TA and DGEBA are utilized without the MEK and dried at 80_{o}C overnight, the molecules react at lower temperature than previously seen in literature resulting in a material with increased T_g as compared to control phenol samples.

5.7 Acknowledgements

This material is based upon work supported by the National Science Foundation Graduate Research Fellowship under Grant Number DGE-1333468. Researchers were additionally supported in this work through the National Science Foundation-Integrative Graduate Education and Research Traineeship: Sustainable Electronics Grant (Grant Number 1144843).

5.8 References

1. Kuruppalil, Z. In *Green Plastics: An Emerging Alternative for Petroleum Based Plastics?*, IAJC-ASEE International Conference, Hartford, Connecticut, Hartford, Connecticut, 2011.
2. Kuruppalil, Z. In *Plastics packaging: the challenge of going green*, The First International Conference on Green and Sustainable Technology, University of North Carolina A&T, University of North Carolina A&T, 2011.
3. Mwanza, B. M.; Mbohwa, C., Drivers to sustainable plastic solid waste recycling: a review. *Procedia Manufacturing* **2017,** *8*, 649-656.
4. Peng, L.; Deng, Y.; Yi, P.; Lai, X., Micro hot embossing of thermoplastic polymers: a review. *Journal of Micromechanics and Microengineering* **2014,** *24*, 1-23.
5. Chen, Z.; Yang, F.; Meguid, S., Multi-level modeling of woven glass/epoxy composite for multilayer printed circuit board applications. *International Journal of Solids and Structures* **2014,** *51* (21-22), 3679-3688.
6. Haugan, E.; Per Dalsjo, P., Characterization of the material properties of two FR4 printed circuit board laminates. FFI Rapport, 2014.
7. Composite Adhesives Market by Resin (Epoxy, Polyurethane), Component (One-Component, Two-Component), Application (Automotive & Transportation, Marine, Aerospace, Wind Energy), and Region - Global Forecast to 2022. (accessed October 4).
8. Bourguiba, A.; Dhaoui, W.; Ghorbel, E., Selection of thinner for epoxy–amine system used as binder for polymeric mortars. *Journal of Applied Polymer Science* **2016,** *133* (39), n/a-n/a.

9. Hong, I.-K.; Yoon, Y. S.; Lee, S.-B., Selection of thinner for epoxy type resins for neon transformer housing. *Journal of Industrial and Engineering Chemistry* **2012,** *18* (6), 1997-2003.

10. Craft, E. Trade secret thinning epoxy: Best practice guidance for reducing the viscosity of epoxy. (accessed February 17).

11. Burkinshaw, S. M.; Bahojb-Allafan, B., The development of a metal-free, tannic acid-based aftertreatment for nylon 6,6 dyed with acid dyes. Part 4: tannic acid. *Dyes and Pigments* **2004,** *62* (2), 159-172.

12. Ontiveros-Ortega, A.; Espinosa-Jiménez, M.; Chibowski, E.; González-Caballero, F., Effect of Tannic Acid on the Surface Free Energy of Polyester Dyed with a Cationic Dye. *Journal of Colloid And Interface Science* **1998,** *199* (1), 99-104.

13. Fei, X.; Wei, W.; Zhao, F.; Zhu, Y.; Luo, J.; Chen, M.; Liu, X., Efficient toughening of epoxy-anhydride thermosets with a biobased tannic acid derivative. *Acs Sustainable Chemistry & Engineering* **2017,** *5* (1), 596-603.

14. Xia, Z.; Kiratitanavit, W.; Facendola, P.; Thota, S.; Yu, S.; Kumar, J.; Mosurkal, R.; Nagarajan, R., Fire resistant polyphenols based on chemical modification of bio-derived tannic acid. *Polymer Degradation and Stability* **2018,** *153*, 227-243.

15. Lang, X. L.; Shang, K.; Wang, Y.; Schiraldi, D., Low flammability foam-like materials based on epoxy, tannic acid, and sodium montmorillonite clay. *Green Mater.* **2015,** *3* (2), 43-51.

16. Shibata, M.; Nakai, K., Preparation and Properties of Biocomposites Composed of Bio-Based Epoxy Resin, Tannic Acid, and Microfibrillated Cellulose. *Journal of Polymer Science Part B-Polymer Physics* **2010,** *48* (4), 425-433.

17. Korey, M.; Mendis, G. P.; Youngblood, J. P.; Howarter, J. A., Tannic acid: A sustainable crosslinking agent for high glass transition epoxy materials. *Journal of Polymer Science Part A: Polymer Chemistry* **2018,** *56* (13), 1468-1480.

18. He, Q.; Yao, K.; Sun, D.; Shi, B., Biodegradability of tannin-containing wastewater from leather industry. *Biodegradation* **2007,** *18* (4), 465-472.

19. Wang, H.; Qu, Y.; Li, D.; Ambuchi, J. J.; He, W.; Zhou, X.; Liu, J.; Feng, Y., Cascade degradation of organic matters in brewery wastewater using a continuous stirred microbial electrochemical reactor and analysis of microbial communities. *Scientific Reports* **2016,** *6*, 27023.

20. Sun, C. T.; Li, Y.; Zhang, Q.; Xue, Z. H., Combination of chelate precipitation and advanced oxidation for treating tannic acid lead wastewater. *Zhongbei Daxue Xuebao (Ziran Kexue Ban)/Journal of North University of China (Natural Science Edition)* **2015,** *36* (2), 182-187.

21. Prigione, V.; Trocini, B.; Spina, F.; Poli, A.; Romanisio, D.; Giovando, S.; Varese, G., Fungi from industrial tannins: potential application in biotransformation and bioremediation of tannery wastewaters. *Applied Microbiology and Biotechnology* **2018,** *102* (9), 4203-4216.

22. Wei, L., Online Determination of Trace Amounts of Tannic Acid in Colored Tannery Wastewaters by Automatic Reference Flow Injection Analysis. *Journal of Automated Methods & Management in Chemistry* **2010**.

23. Sigma-Aldrich Tannic Acid ACS Reagent. http://www.sigmaaldrich.com/catalog/product/sial/t0125?lang=en&region=US (accessed August 3).

6. METAL-TANNATES: SUSTAINABLE ANTI-CORROSIVE PIGMENTS FOR WATERBORNE EPOXY

This work is to be submitted to a journal at a later date. The work itself was done in collaboration with my advisors, but I performed all of the sample preparation, sample analysis, and data analysis for this work on my own.

6.1 Introduction

Corrosion is defined as the chemical reactions and physiochemical interactions between a metal or metal alloy and its environment that result in changes to the properties of the metal.[1, 2] In 2014, corrosion was estimated to cost 276 billion USD annually in the US, which was approximately 3.1% of the gross domestic product (GDP) of the nation.[3] Additionally, it is estimated that 25% of this cost could be avoided with proper methods.[4] This is not a problem for the US alone, as it is a challenge for many Western countries.[2] It introduces costs in many industries including infrastructure, transportation, utilities, manufacturing, and many others.[3] Furthermore, in addition to the economic costs and technological delays, corrosion can cause dramatic consequences for humans and the environment.[5] For this reason, there is tremendous drive to find novel methods to prevent corrosion in many applications.

Corrosion protection refers to the optimization of factors that prevent corrosion. From the literature, the most prominent method for the prevention of corrosion is through coating the surface of the material with anti-corrosive paints.[2] Anticorrosive paint is a mixture including pigments (insoluble particles) which though one method or another prevent or delay the substrate from corroding. Anticorrosive coatings typically consist of multiple layers: 1) a primer, 2) one or several intermediate coats, and 3) a topcoat.[6] The primer's main functionality is to protect the substrate from corrosion, the intermediate layers build up the thickness of the coating, and the top coat to prevent weathering and provide color/gloss.[2] Anticorrosive coatings traditionally contained a large amount of organic solvents, but recent international and national legislation – with the aim of reducing the emission of volatile organic compounds (VOCs) from coatings – has led to significant changes in their formulation.[2] Recent strategies have been to develop coatings with high solid contents, powder coatings, or waterborne coatings with low amounts of organic solvents.[2] While the first two solutions have proven effective, it has proven quite difficult to substitute waterborne coatings for solvent-borne, especially in harsh environments.

Anticorrosive coatings are traditionally classified in 3 ways: 1) barrier effect, 2) inhibitive effect, 3) galvanic effect, and 4) some combination thereof.[2] Barrier effects form a barrier to the diffusion of ions to the surface of the rmaterial, inhibitive coatings passivate the substrate through the build-up of insoluble metallic complexes, and galvanic coatings provide a more electrochemically active coating than the substrate resulting in a sacrificial layer. Combinations thereof provide additional, often synergistic effects and can greatly reduce the corrosion rate of a substrate.

Barrier effect coatings traditionally contain inert pigmentation, such as TiO_2, FeO, or glass flakes at lower pigment volume concentrations with the thickness of the coating playing a large role in the permeability of ions and the resulting properties of the coating.[2, 7] Epoxy and urethane coatings are traditionally utilized for this application, though their hydrophobicity is often a limitation in their adhesion to the metal substrate. Cathodic protection is sometimes used to supplement barrier coatings through the use of a sacrificial anode (e.g. galvanic inhibitors) and are most often utilized in off-shore applications.[2] Sacrificial anodes that are often utilized are aluminum due to its high current output (offshore structures), zinc where risk for passivation of aluminum is higher (e.g. buried pipelines offshore), and magnesium for steel structures in soil and hot water tanks due to its higher driving voltage.[2] Industry has additionally adopted the use of impressed current to circumvent this challenge which is favorable due to its lower cost, but is currently less utilized than sacrificial anode coatings at this time.

A major limitation of these anticorrosive pigments is often that they have known toxicity and that transition to waterborne systems has proven difficult.[8-10] Researchers have developed many less toxic anticorrosive pigments for epoxy coatings. Most recently, strontium aluminum polyphosphate,[8] zinc aluminum phosphate,[11] and zinc acetate-chicorium, [12] methoxy-tolidine and salicylaldehydes,[13] and other biologically-sourced compounds, such as graphene and lignin,[14] and metal tannate complexes,[10] have been explored as anti-corrosive additives in these systems. However, there is yet to be developed a biologically-sourced anticorrosive additive that in waterborne epoxy coatings provides similar functionality to those currently commercially available in solvent-borne epoxy coatings, such as titanium dioxide. Furthermore, while there is a wealth of literature in many biologically-sourced additives, metal-tannate complexes have only been recently explored as a functional additive to this system.

Tannic acid (TA) is a bio-based high molecular weight organic, aromatic molecule that has been found to increase thermal stability, thermomechanical properties, and flame retardancy of many polymer matrices when used as an additive.[15-21] Although it is biologically sourced, TA is a pollutant in industrial wastewater streams, and there is desire to find applications in which to downcycle this molecule after extraction from these streams.[22-26] Tannins have been utilized industrially for decades to prevent corrosion of internal parts of boilers and water cooling systems. Tannic acid has been found to complex with iron (III) ions in solution resulting in stable, self-assembling nanoparticles which is (and has been) utilized in inks and dyes and is currently being explored for its use in medical imaging.[27, 28] However, it is known that TA will complex many metal ions in water solution including Fe[27-29], Cu[30], Mg[10], Al[31], Ag[32], Zn[10], and many others. This research shows how TA can be damaging to the environment when highly concentrated in leather tanning wastewater[22] but potentially appropriate to the filtration of metal ions from other wastewater streams. However, due to their low metal content and potential anti-corrosive potential, these metal-tannate complexes show promise as anti-corrosive additives.

Previous researchers have utilized metal-tannate complexes as anti-corrosive additives in solvent-borne epoxy systems. Previous researchers have utilized magnesium tannate, and zinc tannate in solvent-borne epoxy and showed the potential for these additives to work.[10] Previous researchers have synthesized aluminum and cupric tannate for the purpose of producing a antifouling coating but did not explore the corrosion inhibition of these coatings.[30, 31] However, to the best of the authors' knowledge, due to the compatibility limitation of metal-tannates in water there has been no previous work in metal-tannate complexes as waterborne epoxy anticorrosive additives and no comprehensive review has been done in this space.

The goal of this work was to find ways to synthesize Fe^{2+}, Fe^{3+}, Cu, Mg, Al, and Zn- tannate metal complexes and disperse them in commercially-available waterborne epoxy coatings. These metals were chosen due to their different reduction potentials (Table 6.1). The material properties including thermal stability were studied. The result of this work is that specific components of metal-TA complexes resulted in different material and coating properties.

6.2 Methods

6.2.1 Materials

TA, triethylene tetramine (TETA) and MEK were purchased from Sigma Aldrich (St. Louis, MO, USA). EPON 825 (DGEBA) resin was purchased from Hexion, Inc. (Louisville, KY, USA). Mold Max 60 silicone precursor and initiator – parts A and B - were purchased from Smooth-On, Inc. (Macungie, PA, USA). 20mL borosilicate scintillation vials were purchased from Thermo Fisher Scientific (Waltham, MA, USA).

6.2.2 Preparation of Metal-Tannates

Seven metal tannates were prepared to study a catalogue of reduction potentials (Table 6.1). Samples were prepared using the below procedures.

Table 6.1: Literature derived reduction potential of ions of interest for this study.

Metal Ion Reduction Chemistry	Reduction Potential (V)
$Fe^{3+} + e^- \longrightarrow Fe^{2+}$	+0.77
$Cu^{2+} + 2e^- \longrightarrow Cu$	+0.34
$Fe^{3+} + 3e^- \longrightarrow Fe$	-0.04
$Fe^{2+} + 2e^- \longrightarrow Fe$	-0.45
$Zn^{2+} + 2e^- \longrightarrow Zn$	-0.76
$Al^{3+} + 3e^- \longrightarrow Al$	-1.66
$Mg^{2+} + 2e^- \longrightarrow Mg$	-2.37

Aluminum Tannate (AlT)

40 mL of a 1M $Al_2(SO_4)_3$ in distilled water was added to a 1000 mL solution of 20% TA in distilled water. The pH of the solution was adjusted to 8.0 and was stirred for 1 hour. After stirring, the solution was centrifuged for 60 minutes at 2000 rpm and then the supernatant was removed.

Cupric Tannate - CuT

40 mL of a 1M $CuSO_4$ solution in distilled water was added to a 1000 mL solution of 20% TA in distilled water. The pH of the solution was adjusted to 8.0 and was stirred for 1 hour. After stirring, the solution was centrifuged for 60 minutes at 2000 rpm and then the supernatant was removed.

Ferrous Tannate - Fe(II)T

40 mL of a 1M $FeCl_2$ solution in distilled water was added to a 1000 mL solution of 20% TA in distilled water. The pH of the solution was adjusted to 8.0 and was stirred for 1 hour. After stirring, the solution was centrifuged for 60 minutes at 2000 rpm and then the supernatant was removed.

Ferric Tannate - Fe(III)T

40 mL of a 1M $FeCl_3$ solution in distilled water was added to a 1000 mL solution of 20% TA in distilled water. The pH of the solution was adjusted to 8.0 and was stirred for 1 hour. After stirring, the solution was centrifuged for 60 minutes at 2000 rpm and then the supernatant was removed.

Magnesium Tannate - MgT

40 mL of a 1M $Mg_2(SO_4)_3$ solution in distilled water was added to a 1000 mL solution of 20% TA in distilled water. The pH of the solution was adjusted to 8.0 and was stirred for 1 hour. After stirring, the solution was centrifuged for 60 minutes at 2000 rpm and then the supernatant was removed.

Zinc Tannate - ZnT

40 mL of a 1M $Zn(CH_3CO_2)_2$ solution in distilled water was added to a 1000 mL solution of 20% TA in distilled water. The pH of the solution was adjusted to 8.0 and was stirred for 1 hour. After stirring, the solution was centrifuged for 60 minutes at 2000 rpm and then the supernatant was removed.

All metal tannate samples were dried at 80°C overnight and sieved using a 250µm sieve.

6.2.3 Pigment Characterization

Attenuated total reflectance (ATR) Fourier transform infrared (FTIR) spectroscopy was performed using a PerkinElmer Spectrum 100 FTIR Spectrometer (PerkinElmer, Seer Green, Beaconsfield, UK) outfitted using a zinc selenide (ZnSe) crystal. Samples were scanned from 650 cm$_{-1}$ to 4000 cm$_{-1}$ in transmissive model. Absorbance values were calculated using Spectra (PerkinElmer, Seer Green, Beaconsfield, UK) and were averaged between samples.

Thermogravimetric analysis (TGA) was performed with a Q50 thermogravimetric analyzer (TA Instruments, Newcastle, DE, USA). Samples were prepared for TGA analysis by shaving off sample from epoxy products. Experiments were performed in nitrogen with a 60 mL/min flow rate using a 15 °C/min heating rate from 30 °C to 900 °C. Three samples were run at each concentration and results were averaged. T_d was determined by finding the peak of the mass loss rate curve using Universal Analysis (TA Instruments, Newcastle, DE, USA) and averaging the temperature values at this point.

Statistical analysis was performed using JMP (SAS Institute, Cary, NC, USA). A student's t-test was run to compare samples. A p-value <0.05 was used to indicate statistically significant differences between samples. Regression analysis was performed using OriginPro 2017 (OriginLab Inc., Northampton, MA, USA). Results were fit to an exponential decay and linear models, and the reported equations and standard error (S_e) values were output by the software after regression analysis. S_e values <0.05 were determined as appropriate fits for the regression.

6.2.4 Coating and Sample Preparation

Waterborne resins and sieved additives and 5mL of distilled water were added to a Nalgene container. The Nalgene container was sealed and placed in the FlackTek SpeedMixer using the 400 max-100 holder for a 3 minute mix at 2000 rpm. Steel samples were prepared by degreasing with acetone, polishing with #320 paper and degreased again. The hardener phase was then added to the mixtures and it was mixed on the flacktek for an additional 3 minutes. Samples were then brushed with the paints.

6.2.5 Corrosion Testing

Steel samples of 1 cm^2 were prepared from bulk using a hole saw. In order to isolate the testing apparatus, steel samples were secured to the top of an epoxy cylinder containing a copper wire. Contact was maintained between the copper wire and the sample with the use of crystalbond. Samples were submerged into a 1L solution of 3.5% NaCl at 21°C.

6.3 Results and Discussion

Metal-tannate powders were synthesized and can be visualized (Figure 6.1).

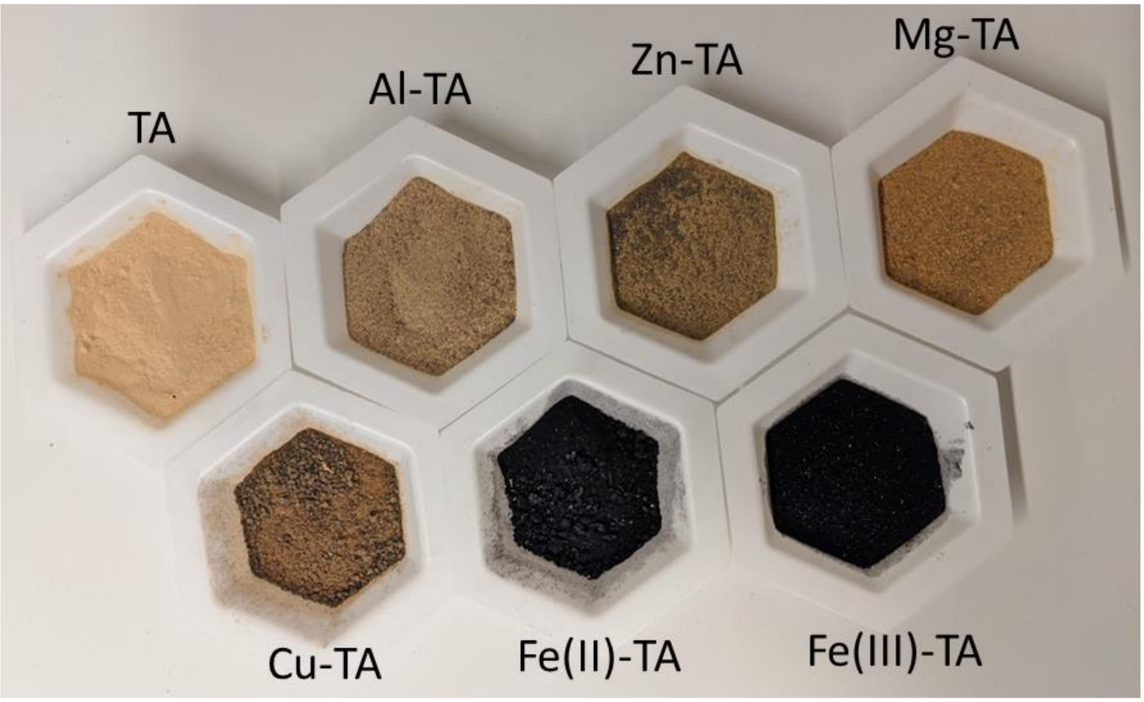


Figure 6.1: Metal-tannate powders visualized after drying.

The resulting dried powders showed distinct colors. Tannic acid is a tan color. AlT samples were slightly darker brown in color. ZnT samples were even darker. MgT samples were redder in color. CuT samples were dark brown. Fe(II) and Fe(III) samples were darkest and comparable in color to each other.

Powders were additionally analysed using FTIR (Figure 6.2). Previous researchers have shown that a change in the peak at 3250 cm^{-1} (phenolic bond stretch) is indicative of metal-tannate complexation. However, in this study all samples containing metal ions there was additionally a change in the peak structure at 1510 cm-1 (phenyl C=C stretch). This result indicated a change in the phenyl bond structure and the phenolic bonds in the TA molecule. The rest of the bonding indicated on FTIR did not appear to significantly change between samples regardless of whether or not metal ions were used.

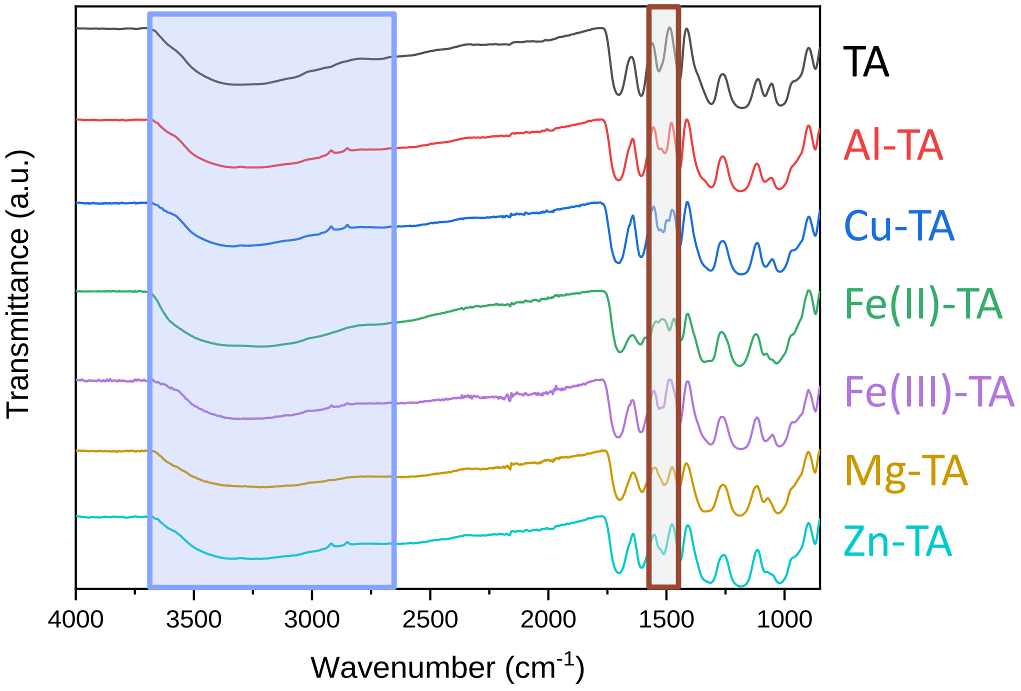


Figure 6.2: FTIR analysis – Metal TA samples. The band at 1510 cm-1 (denoted in red) is indicative of the phenyl bond within the sample. Additionally the peak at 3250 cm-1 (denoted in blue) is indicative of the surface phenol bond on TA.

These results indicated that metal-ions were forming metal-TA complexes as anticipated. Changing the pH of solutions during synthesis deprotinates the phenol -OH bond. This results in a molecule with a stable resonance structure (Figure 6.3). This behavior is unsurprising given the fact that TA is an antioxidant. This results in a molecule with fundamentally changed phenyl bond peaks and fundamentally changed phenol bond peaks. This could explain the changes in the phenyl bond as indicated on FTIR and give further indication that TA-metal complexes have formed.

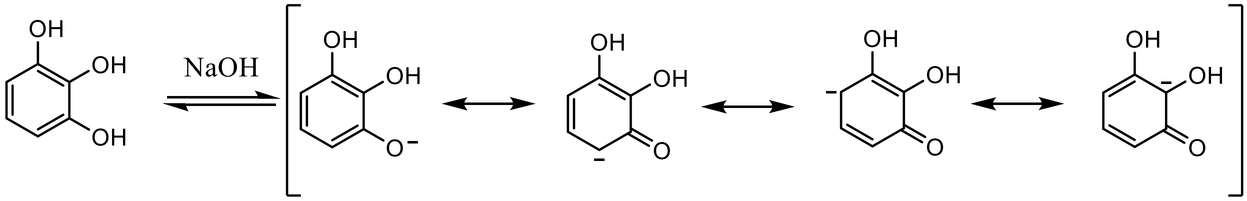


Figure 6.3: Anticipated scheme for deprotination of TA in basic solution which helps explain the bond changing observed in FTIR.

Once verification of metal-TA powder formation was confirmed, the thermal stability of the samples was studied using TGA (Figure 6.4). Results indicated that all samples showed thermal degradation temperatures associated with unmodified TA, though the magnitude of thermal degradation was decreased in each case. The thermal stability of TA-metal complexes were significantly changed as compared to control metal ions alone. For the case of AlT samples, the amount of char remaining at 400°C was higher than control TA alone. While this could be indicative of a more thermally stable char, it could just be because there is more thermally stable metal in the powder which is more thermally stable. The $Al_2(SO_4)_3$ sample shows a thermal degradation temperature at 700C, which is likely the degradation of SO_4. Since TA has replaced the SO_4 in samples, it makes sense that the degradation disappeared. This trend was repeated for all samples except for Zn and Fe samples in which the thermal degradation increased due to the complexation with TA and replacement of less thermally stable Cl^- and acetate ions. These results which indicate that powders trended with thermal degradation of unmodified TA and not the previous ions ionically bonded with the metals further suggests that TA had complexed with the metal ions.

TGA results also indicated that all samples containing metal ions had a decrease in the magnitude of the termal degradation peak associated with TA, which could be because there is more thermally metal ions in solution occupying mass. Although all of the TA is burning away in TGA there remains the original weight of metal ions in the solution. If this were the case, preliminary results indicate that approximately the same amount of metal is contained in each TA-metal complex. All samples burn away to approximately 70 wt% regardless of metal ion used and indicate approximately 20 wt% metal in all samples, assuming the increase in weight is due to metal ion presence alone.

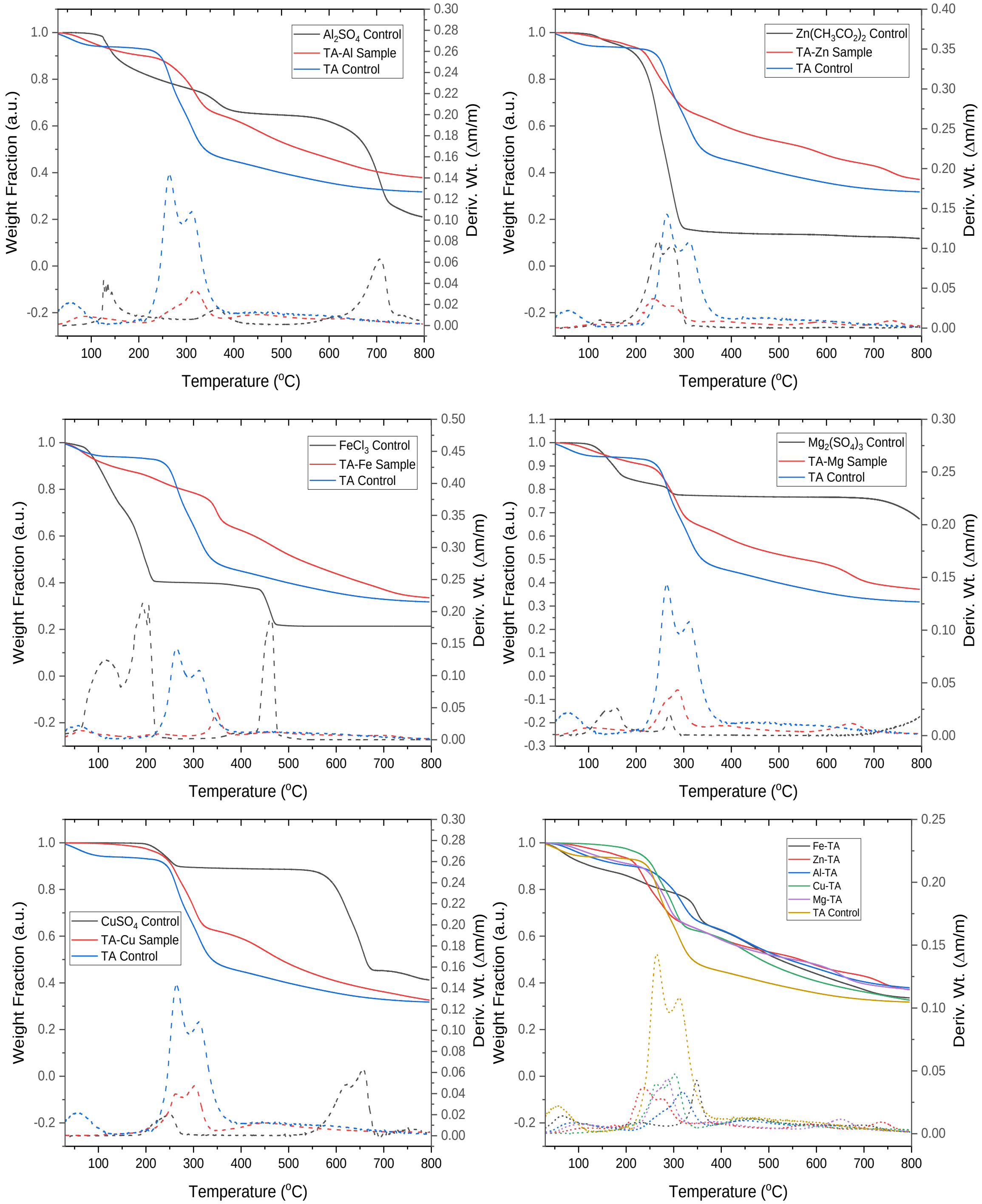


Figure 6.4: TGA thermograms of metal-TA samples.

Waterborne epoxy coatings were developed and visualized (Figure 6.5). All samples, when wet, were opaque. Control samples containin no additives were an off white peach color. Titanium dioxide samples were an opaque white. Aluminum tannate samples were a light brown color. Cupric tannate samples were a forest mint green in color. Ferrous tannate samples were black, and ferric tannate samples were a dark purple-black. Magnesium tannate samples were a reddish brown. Zinc tannate were a dark brown color. All samples showed distinct coloring but overall an opaque dispersion.

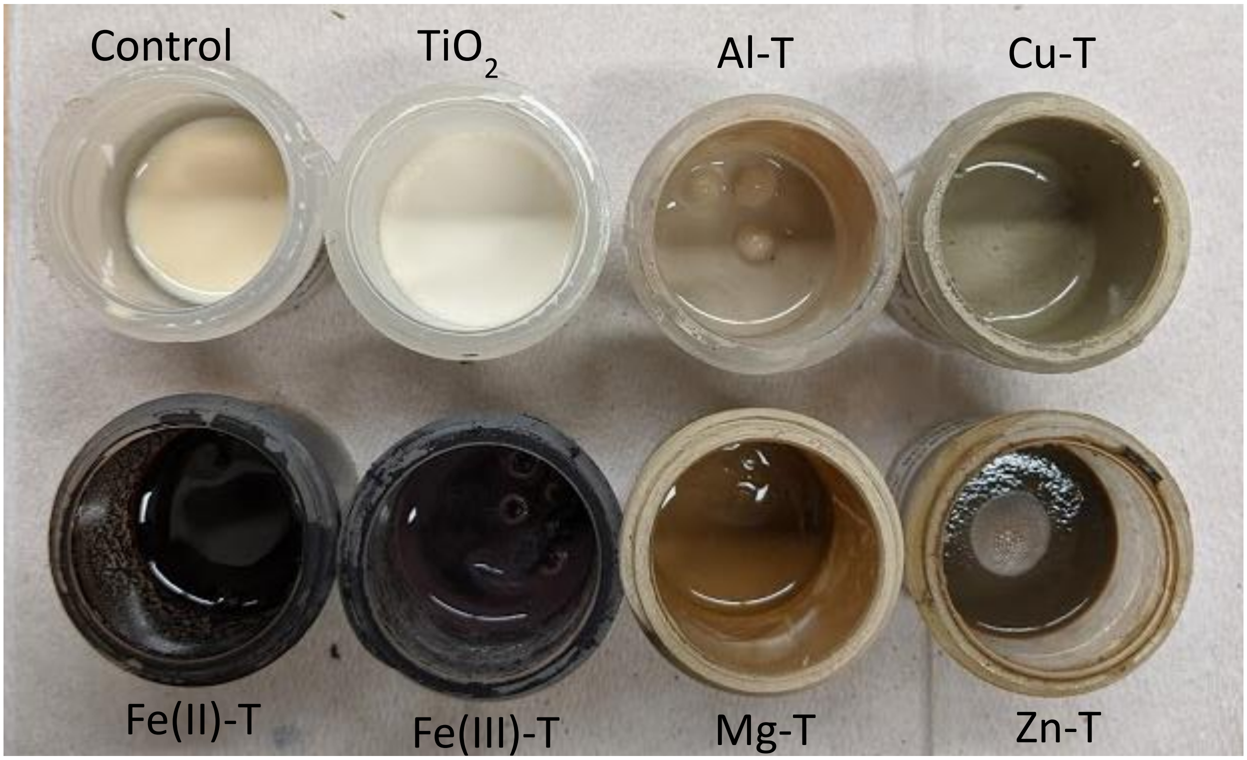


Figure 6.5: Waterborne epoxy paints of metal-TA complexes in solution.

Steel samples were coated with epoxy coatings (Figure 6.6) As can be seen from the figure, the addition of tannates resulted in different adhesive ability of the coating to epoxy. While Titanium Dioxide, Al-T, Fe(II)-T, and Zn-T samples adhered well to the substrate, the Fe(III)-T and Mg-T coatings did not adhere well and flaked off. Cu-T samples flaked only slightly and cracked across the surface.

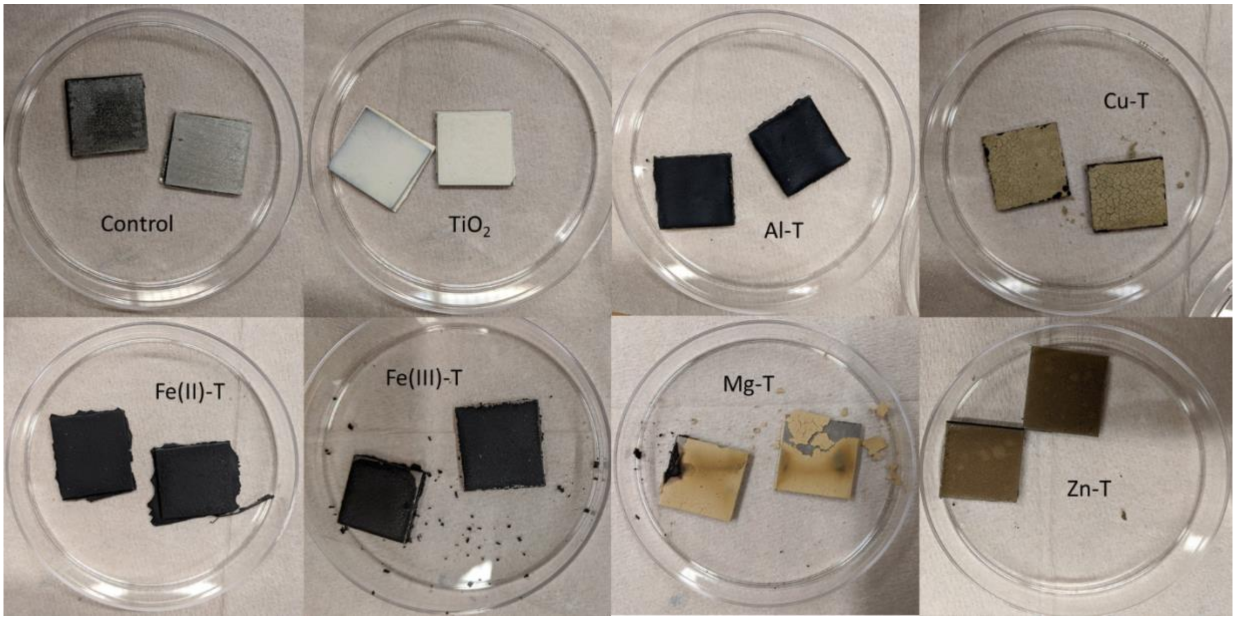


Figure 6.6: Steel samples coated with waterborne epoxy containing different metal-tannates.

6.4 Ongoing Work

Ongoing work is in developing samples for corrosion testing. Samples will be studied using cyclic voltammetry in order to back calculate the corrosion rate using the Tafel plot. A quartz crystal micrograph (QCM) will be utilized to provide the weight loss and change in sample volume during corrosion. Samples will additionally be characterized using a salt-water soak to verify mass loss rate.

6.5 Conclusions

In this work, six metal-tannate powders were synthesized using prior literature to act as anti-corrosive pigments for waterborne epoxy. Coatings were developed using the pigments and a commercially-available waterborne epoxy coating. Al-, Fe(II)-, and Zn-TA coatings were the best performing upon visual inspection. Samples will be tested to measure the corrosive properties. It is expected that metal-TA pigments will change the corrosion rate as compared to the waterborne epoxy control. Samples will be compared to TiO_2, a known anti-corrosive pigment currently utilized in waterborne epoxy systems.

6.6 Acknowledgements

This material is based upon work supported by the National Science Foundation Graduate Research Fellowship under Grant Number DGE-1333468. Researchers were additionally supported in this work through the National Science Foundation-Integrative Graduate Education and Research Traineeship: Sustainable Electronics Grant (Grant Number 1144843).

6.7 References

1. Jones, D., *Principles and Prevention of Corrosion*. 1992; p 568.
2. Sørensen, P.; Kiil, S.; Dam-Johansen, K.; Weinell, C., Anticorrosive coatings: a review. *Journal of Coatings Technology and Research* **2009,** *6* (2), 135-176.
3. Anonymous, NACE International Commences Global Study on Corrosion Costs and Preventive Strategies. *Materials Performance* **2014,** *53* (1), 84.
4. Sastri, E.; Ghali, M.; Elboujdaini, M., *Corrosion Prevention and Protection: Practical Solutions*. John Wiley & Sons, Ltd: 2012.
5. Pandey, M. D.; Nessim, M. A., Reliability-based inspection of post-tensioned concrete slabs. *Canadian Journal of Civil Engineering* **1996,** *23* (1), 242-249.
6. Kjernsmo, D.; Kleven, K.; Scheie, J., *Corrision protection: inspector's book of reference*. U. St.: Hempel A/S: 2003.
7. Kittelberger, W.; Elm, A. C., DIFFUSION OF SODIUM CHLORIDE THROUGH VARIOUS PAINT SYSTEMS. *Industrial & Engineering Chemistry* **1952,** *44* (2), 326-329.
8. Naderi, R.; Attar, M. M., Effect of zinc-free phosphate-based anticorrosion pigment on the cathodic disbondment of epoxy-polyamide coating. *Progress in Organic Coatings* **2014,** *77* (4), 830-835.
9. Roselli, S.; Bellotti, N.; Deyá, C.; Revuelta, M.; Del Amo, B.; Romagnoli, R., Lanthanum-exchanged zeolite and clay as anticorrosive pigments for galvanized steel. *Journal of Rare Earths* **2014,** *32* (4), 352-359.
10. Zmozinski, A. V.; Peres, R. S.; Freiberger, K.; Ferreira, C. A.; Tamborim, S. M. M.; Azambuja, D. S., Zinc tannate and magnesium tannate as anticorrosion pigments in epoxy paint formulations. *Progress in Organic Coatings* **2018,** *121*, 23-29.
11. Darvish, A.; Naderi, R.; Attar, M. R. M., Improvement in polyurethane coating performance through zinc aluminium phosphate pigment. *Pigment & Resin Technology* **2016,** *45* (6), 419-425.

12. Sanaei, Z.; Shahrabi, T.; Ramezanzadeh, B., Synthesis and characterization of an effective green corrosion inhibitive hybrid pigment based on zinc acetate-Cichorium intybus L leaves extract (ZnA-CIL.L): Electrochemical investigations on the synergistic corrosion inhibition of mild steel in aqueous chloride solutions. *Dyes and Pigments* **2017,** *139*, 218-232.

13. Wahba, O. A. G.; Hassan, A. M.; Naser, A. M.; Hanafi, A. M. G., Green synthesis and spectroscopic studies of some complexes compounds as pigments and their applications in paints. *Pigment & Resin Technology* **2017,** *46* (4), 286-295.

14. Wang, S.; Hu, Z.; Shi, J.; Chen, G.; Zhang, Q.; Weng, Z.; Wu, K.; Lu, M., Green synthesis of graphene with the assistance of modified lignin and its application in anticorrosive waterborne epoxy coatings. *Applied Surface Science* **2019,** *484*, 759-770.

15. Burkinshaw, S. M.; Bahojb-Allafan, B., The development of a metal-free, tannic acid-based aftertreatment for nylon 6,6 dyed with acid dyes. Part 4: tannic acid. *Dyes and Pigments* **2004,** *62* (2), 159-172.

16. Ontiveros-Ortega, A.; Espinosa-Jiménez, M.; Chibowski, E.; González-Caballero, F., Effect of Tannic Acid on the Surface Free Energy of Polyester Dyed with a Cationic Dye. *Journal of Colloid And Interface Science* **1998,** *199* (1), 99-104.

17. Fei, X.; Wei, W.; Zhao, F.; Zhu, Y.; Luo, J.; Chen, M.; Liu, X., Efficient toughening of epoxy-anhydride thermosets with a biobased tannic acid derivative. *Acs Sustainable Chemistry & Engineering* **2017,** *5* (1), 596-603.

18. Xia, Z.; Kiratitanavit, W.; Facendola, P.; Thota, S.; Yu, S.; Kumar, J.; Mosurkal, R.; Nagarajan, R., Fire resistant polyphenols based on chemical modification of bio-derived tannic acid. *Polymer Degradation and Stability* **2018,** *153*, 227-243.

19. Lang, X. L.; Shang, K.; Wang, Y.; Schiraldi, D., Low flammability foam-like materials based on epoxy, tannic acid, and sodium montmorillonite clay. *Green Mater.* **2015,** *3* (2), 43-51.

20. Shibata, M.; Nakai, K., Preparation and Properties of Biocomposites Composed of Bio-Based Epoxy Resin, Tannic Acid, and Microfibrillated Cellulose. *Journal of Polymer Science Part B-Polymer Physics* **2010,** *48* (4), 425-433.

21. Korey, M.; Mendis, G. P.; Youngblood, J. P.; Howarter, J. A., Tannic acid: A sustainable crosslinking agent for high glass transition epoxy materials. *Journal of Polymer Science Part A: Polymer Chemistry* **2018,** *56* (13), 1468-1480.

22. He, Q.; Yao, K.; Sun, D.; Shi, B., Biodegradability of tannin-containing wastewater from leather industry. *Biodegradation* **2007,** *18* (4), 465-472.

23. Wang, H.; Qu, Y.; Li, D.; Ambuchi, J. J.; He, W.; Zhou, X.; Liu, J.; Feng, Y., Cascade degradation of organic matters in brewery wastewater using a continuous stirred microbial electrochemical reactor and analysis of microbial communities. *Scientific Reports* **2016,** *6*, 27023.

24. Sun, C. T.; Li, Y.; Zhang, Q.; Xue, Z. H., Combination of chelate precipitation and advanced oxidation for treating tannic acid lead wastewater. *Zhongbei Daxue Xuebao (Ziran Kexue Ban)/Journal of North University of China (Natural Science Edition)* **2015,** *36* (2), 182-187.

25. Prigione, V.; Trocini, B.; Spina, F.; Poli, A.; Romanisio, D.; Giovando, S.; Varese, G., Fungi from industrial tannins: potential application in biotransformation and bioremediation of tannery wastewaters. *Applied Microbiology and Biotechnology* **2018,** *102* (9), 4203-4216.

26. Wei, L., Online Determination of Trace Amounts of Tannic Acid in Colored Tannery Wastewaters by Automatic Reference Flow Injection Analysis. *Journal of Automated Methods & Management in Chemistry* **2010**.

27. Smith, C. A.; Paterson, R. A.; Lowe, B. J.; Te Kanawa, R., Consolidation of Black-dyed Māori Textile Artefacts: Evaluating the Efficacy of Sodium Alginate. *Studies in Conservation* **2018,** *63* (3), 139-154.

28. Phiwchai, I.; Yuensook, W.; Sawaengsiriphon, N.; Krungchanuchat, S.; Pilapong, C., Tannic acid (TA): A molecular tool for chelating and imaging labile iron. *European Journal of Pharmaceutical Sciences* **2018,** *114*, 64-73.

29. Wilson, H. L., Investigation into non-aqueous remedial conservation treatments for iron-tannate dyed organic materials. Carr, C.; Rigout, M., Eds. University of Manchester: 2013.

30. Pérez, M.; Blustein, G.; García, M.; Del Amo, B.; Stupak, M., Cupric tannate: A low copper content antifouling pigment. *Progress in Organic Coatings* **2006,** *55* (4), 311-315.

31. Pérez, M.; García, M.; Blustein, G.; Stupak, M., Tannin and tannate from the quebracho tree: an eco-friendly alternative for controlling marine biofouling. *Biofouling* **2007,** *23* (3), 151-159.

32. Wang, T.; Ma, B.; Jin, A.; Li, X.; Zhang, X.; Wang, W.; Cai, Y., Facile loading of Ag nanoparticles onto magnetic microsphere by the aid of a tannic acid—Metal polymer layer to synthesize magnetic disinfectant with high antibacterial activity. *Journal of Hazardous Materials* **2018,** *342*, 392-400.

7. SUMMARY AND FUTURE WORK

7.1 Conclusions

Many, if not all, precursor units and additives in currently commercially available epoxy systems are synthesized from petroleum and have known toxicological impacts on humans and the environment. The primary purpose of this dissertation was to mitigate these challenges. Herein, the biologically-sourced, edible, and generally regarded as safe (GRAS) molecule tannic acid (TA) was introduced to this system in many previously unexplored ways in an effort to mitigate both of the above named challenges for epoxy, with differing amounts of success. The work within this document shows that the primary challenge faced with the introduction of TA to epoxy has been limited compatibility. In this work, several methods previously unexplored in the literature to disperse TA into epoxy matrices to enhance the sustainability of the system were studied. When this dissertation work began, very little literature was available for TA in epoxy. However, it is clear to see that the work herein has inspired several novel studies in this application given more recent citations.

The aim of this dissertation work was to develop novel methods to disperse TA into epoxy to enhance material properties. We believe there have been 5 unique projects regarding the dispersion of TA into epoxy using chemical modification, creative processing techniques, and some combination thereof. The conclusions are explained in more detail below. The unique contributions to science identified in each chapter are identified clearly below with underlined and bolded text within the paragraphs.

7.1.1 Tannic Acid – Alternative Resin for Epoxy

Using high temperature processing techniques, up to 8 wt% TA was dispersed in epoxy resin with good compatibility, and its intumescenct behavior was studied. The results from this study indicate that **adding TA to a DGEBA epoxy resin can not only serve to increase the intumescent behavior of the polymer without significantly impacting the mechanical properties, but it can also decrease the propensity for epoxy resin to crystallize in transit**. Both results indicate that TA has the potential to serve as a biologically sourced, economical replacement to currently available intumescent epoxy additives.

Future work in this area is to explore TA as a hardener for this resin system to develop a fully-TA based epoxy.

7.1.2 Tannic Acid – Alternative Hardener for Epoxy

Currently available epoxy hardening agents have unintended health and environmental impacts. There is a need for an alternative, more sustainable alternative epoxy hardener to be developed that is capable for use industrially, especially in high-temperature applications. Because of its high concentration of crosslinking sites, **TA was found to be able to react with DGEBA resin to form a densely crosslinked epoxy polymer with resulting high thermal stability and thermomechanical properties**, something seen before for TA in previous literature but never at this scale. The resulting thermomechanical properties and T_gs were significantly higher than those previously reported for TETA hardened epoxy, and within the range of several commercially available high T_g epoxy thermosets, such as dicyandiamide and 4,4'-diaminodiphenyl sulfone. The resulting mechanical properties and T_g could be tuned by changing the loading level of TA in the DGEBA resin. The resulting thermosetting materials show promise in a variety of applications. Because the synthesis is simple, it is expected that this process can be easily scaled-up to larger industrial processes in which TA can potentially replace novolac resins in ongoing processes. With an industrially available, comparably priced, more sustainable, and effective epoxy hardening agent available to the market, it is the hope of the authors that this material can be utilized to lessen the health and environmental impacts of epoxy material synthesis.

Future work in this space includes: 1) measure the flame retardancy (as TA is a known flame retardant in many applications) and, 2) degradability (TA is hydrolyzable) of these TA-hardened epoxies.

7.1.3 Tannic Acid – Alternative Flame Retardant for Epoxy

There is a significant need for researchers to develop alternative chemicals to the more toxic flame retardants currently used industrially in epoxy thermosets. In this chapter, biologically-based and non-toxic TA was studied as an alternative compound to these chemicals. In order to combat compatibility concerns and enhance flame retardancy, acetylation was used. The results from this work showed that the degree of acetylation of the molecule had a significant impact on the ability for the molecule to work as a flame retardant and its thermomechanical properties. Higher surface acetylation of TA resulted in a significant reduction of the flame retardant ability at higher loading levels due to the inability for the molecule to interact with the thermoset through crosslinking. Samples that were partially acetylated showed significant reduction in PHR, MLR, and THR which was largely attributed to the presence of residual phenol groups**. The result from this chapter shows that through partial "surface" acetylation the flame retardancy of TA can be enhanced significantly**. It is the hope of the researchers that this chapter could be used to decrease the environmental and health impacts of the use of epoxy thermosets around the world.

Future work in this space includes exploring TA-resin systems with TA hardener and flame retardants to develop a fully TA-based epoxy system.

7.1.4 Tannic Acid – Alternative Thinning Agent Additive for Epoxy

The use of solvent to thin epoxy thermosets is industrially utilized for a variety of applications, but the addition of small amounts of solvent has been found to decrease mechanical properties significantly. **In this work, when dried at room temperature MEK was found to plasticize the epoxy matrix resulting in a thermoset with higher toughness, compression strength, and strain at break. The addition of TA to this system did not make these properties better, but surprisingly instead made them worse.** This could have been because TA and TETA reacted in solution resulting in less crosslink density or because TA additionally plasticizes the matrix. However, for this reason higher loading levels of TA were studied and MEK was driven off using a vacuum oven and heat. When this was performed, **TA was actually found to crosslink into the epoxy matrix but at lower temperature than previously seen in literature (80°C). The**

resulting materials, which were thinned at room temperature, **were found to have high hardness and glass transition temperatures.**

Future work in this space should involve the use of other epoxy hardeners besides amine-based. Additionally, the flame retardancy of these samples should be explored.

7.1.5 Tannic Acid – Alternative Anticorrosive Additive for Epoxy

The use of water- and solvent-borne epoxy systems as anticorrosive coatings for steel has greatly enhanced its corrosion resistance and prevention. However, a major limitation of the anticorrosive pigments currently used is often that they have known toxicity and that transition to waterborne systems has proven difficult. While there is ongoing research in this space, there is yet to be developed a biologically-sourced anticorrosive additive that in waterborne epoxy coatings provides similar functionality to those currently commercially available in solvent-borne epoxy coatings, such as titanium dioxide. The goal of this work was to develop this coating. This project is still ongoing in the lab as corrosive behaviors of the coatings is still being measured. However, **aluminum-, cupric-, ferrous-, ferric-, magnesium-, and zinc-tannate pigments were synthesized, isolated, and dispersed into waterborne epoxy coatings**, something previously unseen in the literature.

The chemistry involved in developing metal-tannate paints is useful for a variety of applications including 1) flame retardant paints for many substrates including wood and plastic, 2) magnetic material coatings, 3) conductive polymers, and 4) antifouling and antimicrobial coatings. It is the hope that these applications can be additionally explored in future work.

7.2 Final Remarks

This dissertation work has begun what will be the tip of the iceberg with regards to the useful applications of TA in epoxy resin. It is the hope of the author that this document will serve as a starting point and a spark for future work and innovation in this space.

APPENDIX A. COMPARATIVE ENVIRONMENTAL AND SOCIAL LIFE CYCLE ANALYSIS FOR THE PRODUCTION OF ACTIVATED CARBON

This work is based on an article that is currently under review in the *International Journal of Lifecycle Assessment* (IJLCA). For this work, I am listed as first author and I performed the analysis for the environmental section of this work. Kristen Quade, a collaborator on this work, performed the social lifecycle assessment at the end of this work.

A.1 Abstract

Purpose: Activated carbon is sourced mainly from coal, wood, and lignocellulose materials such as coconut husks and is synthesized using a physical (or thermal) activation or chemical activation. While there is not a significant difference in the cost-comparison, it is well known that chemical activation of carbon is a more sustainable process. It is the goal of this assessment to perform a quantitative environmental and social lifecycle analysis of the three source materials and two main synthesis mechanisms. Methods: SimaPro 2017 software and comparative TRACI 2.1 analysis were used for the bulk of the process analysis in this work while SimaPro 2017 Social Hotspot Analysis was used to compare social impacts. The work is divided into three analyses: 1) Raw material extraction and transportation, 2) Activation, and 3) Social impacts of raw material extraction. Results & Discussion: Counterintuitively, due to its high carbon content and yield, chemical activation of coal was found to be the most sustainable process overall and physical activation of coconut husks was found to be the most impactful. Further, based on the assumptions made social life cycle analysis showed that there are significant concerns with all three industries' methods of obtaining source materials, but of the three processes coal was found to have the least social impact overall. Conclusions & Suggestions: Sourcing-driven analysis indicated that comparatively speaking the coconut husks had the highest environmental impact. Process-driven analysis showed that for physical activation coal seemed to have the largest impact in specific categories while wood and coconut had the largest impact for the other categories that were considered for this analysis. Social –driven analysis indicated that all the materials have serious negative social impacts overall.

A.2 Introduction

Activated carbon-based water filters are becoming increasingly more commonplace in the average American home. In fact, more than 40% of Americans use a home water treatment unit which can cost from less than \$20 to as much as \$500 depending on the manufacturer of the device (EPA 2005). Activated carbon is a form of processed coal which has a high surface area to volume ratio to enable adsorption of large amounts of impurities onto the surface or to facilitate chemical reactions on the surface (Dillon 1989). Because the surface of activated carbon is the active region, there has been a significant amount of research developing the processes to enable maximum surface area post-production. Currently, just one gram of industrially-produced activated carbon has a surface area in excess of 3,000 m_2 (Dillon 1989). It contains a large number of small pores throughout the material that can range from below 10 nm (micropore) in size to between 10 and 100 nm (mesopore), to greater than 100 nm (macropore) depending on the processing method (Spencer 2017). The pore size often indicates the ability of the material to adsorb chemicals onto the surface, with smaller pores desired for most gas-filtration based industrial applications and larger pores for liquid-filtration based (Activated Carbon Solutions 2017). However, a broad range of pore sizes is necessary in point of use water-filtration devices in order to allow for movement of adsorbates through the carbon pores and for the adsorption of particular molecular sizes (Activated Carbon Solutions 2017).

Activated carbon works as an adsorptive surface because the large internal surface area has several attractive forces for many types of impurities in water systems. Attraction of the carbon surface for dissolved adsorbates is only possible if the attractive forces to the surface of the activated carbon are stronger than the attractive forces that keep them dissolved in solution (Spencer 2017). Such molecules include organic compounds, components with high molecular weights, and neutrally-charged compounds (Spencer 2017). Because of this ability, activated carbon, while most notably used for household water purification, is also used in power plant and landfill gas emission purification, medications, food and beverage processing, precious metal recovery, and volatile organic compound (VOC) removal and odor control in industrial processes (EPA 1974, USDA 2002, USDA 2002, Bourke 1989). Global demand for activated carbon was 1.7 million metric tons in 2016, with 36% of the market coming from Asia and another 36% of the market in North America (Zhang 2007). The market is expected to expand to 2.1 million tons in 2021 due to the increase in residential and industrial demand for the product in Asian and North American markets (Zhang 2007). The reason for the high demand in North America is due to federal regulations on the removal of mercury at coal-fired power plants, cement kilns, and industrial boilers to prevent the formation of disinfection byproducts in drinking water (Zhang 2007). Due to the health of the Asian market currently, industrial processes in Asia are driving the demand in this part of the world (Zhang 2007).

Activated carbon can be created from a variety of different sources but the main requirement is that the material must contain a high carbon content to provide high yield (Spencer 2017). The main industrial sources of activated carbon are from wood-based products and coal which encompass 31% and 64% of the market respectively; however, more recent research has determined that coconut husks are a more natural source of activated carbon and it is being pursued by various industries - the manufacturers of point of use water filtration devices (Zhang 2007). This is due largely in part to ongoing federal regulation world-wide to minimize the use of coal in a variety of applications. Coal-based activated carbon is largely exported from China where the mining industry is mainly composed of underground mines, many of which are illegal and run without meeting regulations mandated by the government (International Tropical Timber Association 2005). Wood-based activated carbon is largely exported from Venezuela from large tree-plantations where worker-safety hazards have lasting impacts on the individuals in the industry (White 1997). Coconut shell-based activated carbon is largely exported from Indonesia where concerns about land ownership dynamics cause social impacts (Hernandez 2014). Currently, coconut shell-based activated carbon demands the highest price in the market space, costing over 1500 USD per ton, while coal-based products cost only 750 USD per ton (Zhang 2007). The price of coconut shell-based products has been falling since July 2016 because of enhanced supply capacity and fiercer market competition (Zhang 2007).

To the best of the authors' knowledge, there has been no comparative research on the lifecycle of coal, wood, and coconut husk to produce activated carbon as well as the physical/chemical activation pathways of each material. Further, there has been no previous comparative work done on the social sustainability of the three sourcing materials either. It is the goal of this assessment to do a comparison between the three main source materials of activated carbon for water filtration

- coal, wood, and coconut shells - and compare the two main methods of activation - physical and chemical activation - to determine which method is the most sustainable. A cradle-to-gate comparative life cycle assessment (LCA) was performed including both environmental and social life cycle assessment.

A.3 Methods

SimaPro 2017 software was used for the bulk of the process analysis in this work while SimaPro 2017 Social Hotspot Analysis was used to compare social impacts. The work is divided into three analyses: 1) Raw material extraction and transportation, 2) Activation, and 3) Social impacts of raw material extraction. For the purposes of this assessment, the functional unit for the raw material extraction and transportation was defined as 1 kg of resultant material. This value was determined as it was observed in the literature for a variety of source materials and to keep the work consistent with literature the authors maintained this functional unit. Regarding the activation pathway, the functional unit was defined as 110 tons of activated carbon, which included the raw material extraction and transportation scaled-up to this value, which was found to be the daily throughput of activated carbon using a coal pulverizer, another value determined from the literature. For social impacts of raw material extraction, the functional unit was defined as labor hours impacted by the production of one United States Dollar (USD) value. Comparative TRACI 2.1 analysis was used to compare the individual processes as well as individual process analyses. To evaluate environmental impact of all processes associated with the procurement of raw material TRACI 2.1 was used with Simapro. The specific aspects of analysis for each raw material extraction method can be found in the supplemental information for this work.

A.4 Results and Discussion

A.4.1 Raw material extraction

The selection of raw material for activated carbon depends upon the application in which the activated carbon will be used. There are many materials which can be used as feedstock to produce activated carbon. However, the most commonly used raw materials are wood, wood charcoal, peat, lignite and lignite coke, hard coal, bituminous coal, coconut shells, sawdust, plastic residuals etc. (3, 10). Different feedstocks processed under identical conditions yield activated carbons with different physical and chemical properties (Zhang 2007). The same feedstock when processed under different conditions also yields activated carbons having different properties. So, for a particular feedstock, using an appropriate combination of activation procedures and conditioning, we can tailor the resultant activated carbon to have desired physical and chemical properties which are suited to a particular application.

I. Coal

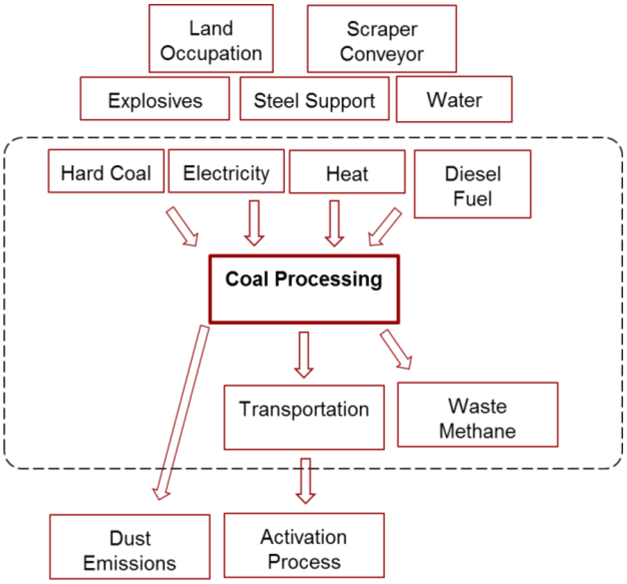


Figure A.1 A visualization of the system boundary for the synthesis of GAC from coal.

Coal is currently the most widely used raw material to produce activated carbon. China is the second largest consumer of activated carbon behind the United States. In 2016, China produced about 400,000 tonnes of coal based activated carbon compared to just 200,000 tonnes of wood based activated carbon (Gratuito 2008). Coal is used more widely because it is easily available with a low cost, sophisticated and fairly reliable supply chain. However, with increasing focus on environmental sustainability, other sources for activated carbon which are supposed to be more environmentally sustainable are being used. It is projected that the demand for coal based activated carbon will decline steadily in coming years as other sources are developed (Gratuito 2008). A representative unit process for coal mining process was created (Figure 1).

The process shown in the figure above is only representative and the actual process may vary from mine to mine. For this study, we have assumed that the coal comes from China as it is the largest producer of coal and has the largest deposits of coal. Around 85% of coal is extracted using underground mining in China (Arena 2016). Several types of coal can be used as raw material for activated carbon production. However, bituminous coal-based products are in greater demand as they have greater density, hardness and abrasion resistance. They are also more durable as compared to other coal-based carbons (Transparency Market Research 2016). We have also assumed that the facility that manufactures activated carbon is located 20 kilometers from the coal processing facility for the purpose of this study. It is assumed that the coal is transported using railways. Further, we have also assumed that many parts of the process including the water usage, explosive usage, and the dust emissions do not contribute significantly to the life cycle of coal

II. Wood

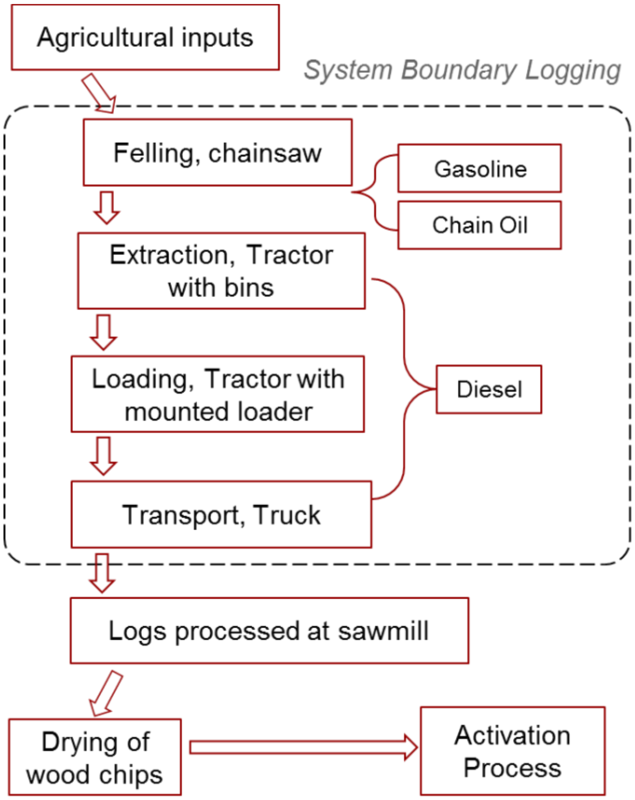


Figure 2. A visualization of the system boundary for the synthesis of GAC from wood products.

An increasing demand for granular activated carbon means the sources of carbon for activation should be diversified to keep up with demand. Wood is one resource used for producing activated carbon. Like coconut shells, wood is often thought of as a sustainable resource unlike coal. The market for wood activated carbon is projected to reach US $ 456 million by 2024 (Transparency Market Research 2016). Increases in government regulations for "airborne mercury emissions from power plants in the U.S. and China is the key driver of the wood activated carbon market" (Hernández 2014). Wood activated carbon is already used by major activated carbon filter producers. The two biggest companies using wood activated carbon are Calgon Carbon Corporation and Cabot Norit Americas Inc. In the National Science Foundation ANSI 61 listings of activated carbon products, both companies have multiple products using carbon sources of wood chips or wood char combined with either carbon sourced from coal or coconut shells. If the wood activated carbon market will continue to grow as projected, it will become increasingly important to understand the impacts associated with using wood as a source of carbon.

The short wood system was assumed as the method of logging in the analysis for the acquisition of wood. The short wood system is suitable for logging in areas which have low inclination. It consists of the tree being felled with a chainsaw. The tree is further processed at the site into smaller logs. These logs extracted from the site. They are bunched, collected, and loaded into bins mounted on a tractor. The logs are brought roadside and unloaded. The logs are then loaded for transport with the aid of a tractor with a mounted loader. For this analysis, the logs are assumed to be transported 20 km by diesel truck (Hernández 2014, Miranda 1998, Laschi 2016, Bruckman 2017, Arena 2016).

The agricultural inputs of wood were not considered within the scope of this analysis (Figure 2). The energy inputs associated with processing the logs into its primary product of timber was not included. This was done because the wood chips and sawdust used in the GAC production is the byproduct of the timber production and otherwise would be a waste product. Furthermore, the maintenance of the chains used with the chainsaw were not included, worker transportation was not included, and it was assumed 1 kg of harvested wood is the same as 1 kg of sawdust or wood chips to be used in the activation process. This assumption underestimates the environmental impacts. The drying of the wood chips was also excluded from the process. The discussion on energy inputs and environmental impacts of this process can be seen in the supplemental information section.

III. Coconut Husk

Although coconut shells comprise a relatively small portion of the activated carbon market, they are often touted as the most sustainable option by the suppliers of the GAC. For the purpose of this LCA, coconuts grown in Indonesia will be considered as the source. Indonesia was chosen as it is the world's largest producer of coconuts (Waney 2002).

Two types of coconut farming occur in Indonesia, traditional and intensive. Traditional farming involves cultivating tall types of coconut tree that grows naturally in Indonesia such as Tenga Tall and Mapanget Tall, which comprise around 95% of the coconuts cultivated (Woodruff 1979). Additionally, during traditional farming, minimal to no chemical fertilizers are implemented during farming. The gestation period for this type of tree is around 6-7 years and can be harvested 3-4 times per year once fully grown. Intensive farming concerns the cultivation of hybrid coconut trees that tend to be shorter in stature as well as faster growing. The two most common varieties are PB 121 and KHINA-1 which were introduced by Smallholder Coconut Development Project in the late 1970's (20). These hybrid coconut varieties have a gestation period of around 5 years and can be harvested up to five times annually. However, the hybrid varieties require a regimented watering and fertilizer application schedule. The most common fertilizers used are lime, triple superphosphate (TSP), urea, and potassium chloride (KCl). Not all these fertilizers are necessarily used in all intensive farming situations but rather the application depends on the soil conditions where the coconut is cultivated. In addition, some combinations of fertilizers are often used to adjust for pH or improve absorption capability of nitrogen from urea or phosphorus from TSP.

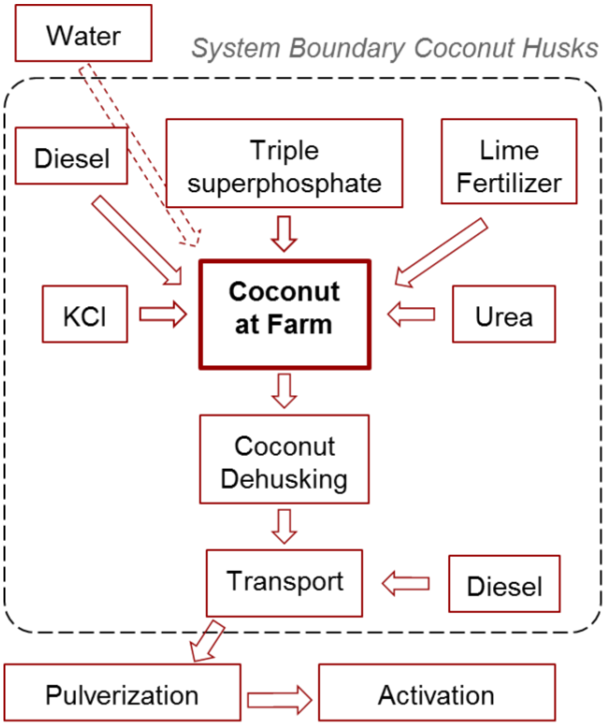


Figure 3. A visualization of the system boundary for the coconut husk sourcing portion of the activation process.

Due to the contract farming typically occurring in Indonesia, coconut farms are around 20 ha or smaller. Farms of this size comprise 95% of the coconut industry in Indonesia (Waney 2002). Because of the small scale on which coconuts are produced, the processing of the coconuts is typically performed by unskilled day laborers on site as opposed to being transported to a factory for processing. Processing in this scenario refers to the separation of the husk from the copra and extraction of milk. Thus, the primary impacts due to coconut production include that from transportation and that of the fertilizers, when used but lacks any sort of mechanical processing.

Several assumptions were made to approximate the process of the farming of Indonesian coconut shells. The urea was approximated using economic allocation based on the liquid urea-ammonium nitrate solution process in Simapro. This process is based on European data when the urea would likely have been produced in China or some other country on the continent of Asia. This is a limitation but for the purposes of this LCA, they are assumed to be approximately equal. There is likely a negligible difference between the European and Chinese urea production processes in comparison with the net environmental burden of the coconut shell production. Similar assumptions were used for the production of triple superphosphate, potassium chloride, and lime.

Additionally, economic allocation was used for the Simapro production of coconut husks process. This is a reasonable assumption as the primary use of the coconuts is for their oil, which is extracted from copra and not the husk. If the husks were not used as a source for activated carbon, they are generally used as a source of fuel. The coconut is assumed to be 17% husk by weight. Additionally, average values for fertilizer application were assumed. A value of 0.0134 kg of TSP was assumed to be needed per 1kg of coconut husk produced. In addition, 0.015 kg Lime, 0.025 kg urea, and 0.029 kg potassium chloride were needed to produce 1 kg of coconut husks (Ahmadpour 1996). Two scenarios were considered in Simapro, first that of traditional farming and second that of intensive farming. For traditional farming, chemical fertilizers included lime and TSP while for intensive farming, urea and potassium chloride were also applied. In the case of intensive farming, the addition of water was neglected as it would likely be sourced from a natural source as opposed to a municipal water purification plant. The assumptions that have been made led to a system boundary that was used for the rest of the calculations (Figure 3).

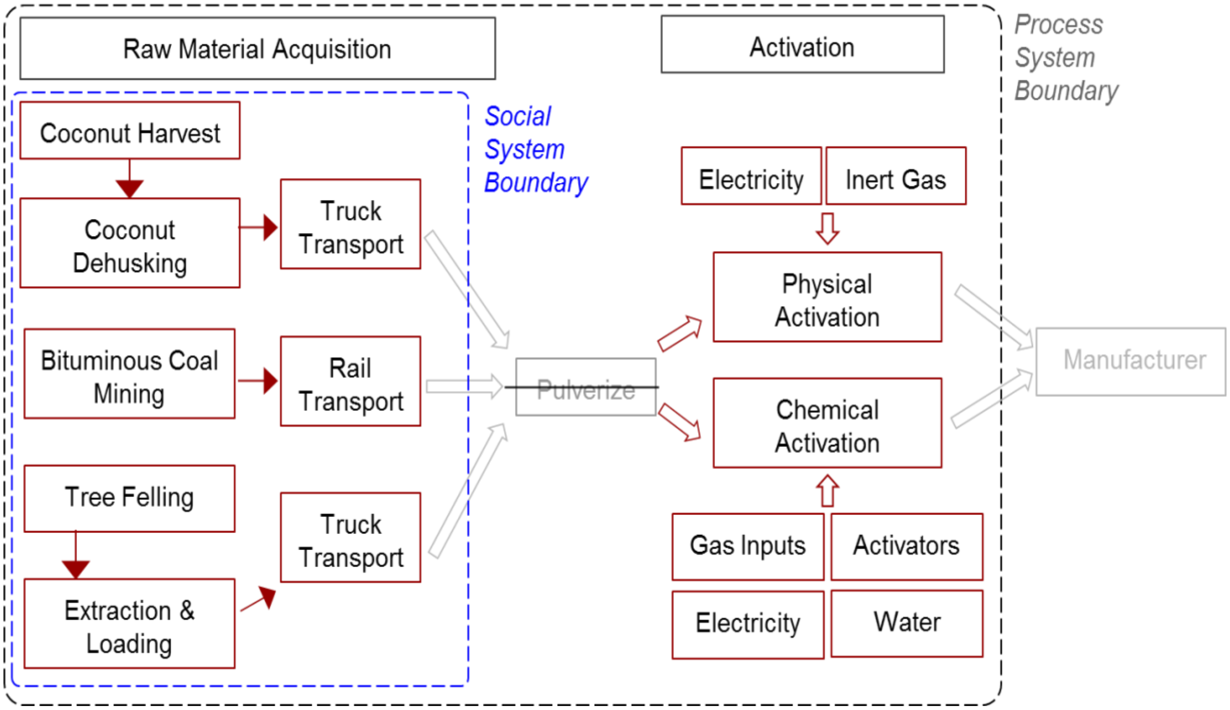


Figure 4. The boundary conditions for the overall process of acquisition and activation of GAC

IV. Impact Assessment of Raw Material Acquisition

A visualization for the comparative analysis of raw material acquisition and activation processes was created (Figure 4). From this analysis, and the above assumptions and review, the comparative analysis was performed and visualized (Figure 5).


Relative Impacts: Bituminous Coal Mining

Relative Impacts: Logging

Relative Impacts: Coconut Husk Harvesting

Comparison of Raw Material Acquisition

Figure 5. Results of quantitative life cycle analysis of coal, wood, coconut, and a comparison of all 3 materials

The analysis for coal processing showed that of the inputs considered the diesel boiler used in the mining process is the largest contributor to the environmental impacts, except for ozone depletion in which case transportation is the largest contributor. In the impacts associated with logging, the noticeable impacts come from the transportation of the logs from the harvest site to the sawmill.

The transportation is the biggest contributor to environmental effects in all categories excluding ecotoxicity and fossil fuel depletion where the use of the tractor contributes over 80% of the impacts. Outside of ecotoxicity and fossil fuel depletion, the largest contributors are the chemical inputs associated with processing and extraction: diesel, gasoline, and chain oil. Looking at the actual magnitudes of impact shows that the biggest impact categories affected by logging are ecotoxicity and fossil fuel depletion. For a better understanding of the magnitudes of each impact associated with logging see the supplemental information section on wood where a table is available.

Due to the lack of traditional agriculture in Indonesia, the bulk of the impact is associated with chemical fertilizers used in intensive farming practices. Liquid urea is responsible for the bulk of this impact in all categories other than carcinogenics, non carcinogenics, and fossil fuel depletion, while TSP, KCl, and lime comprise relatively small portions of the rest of various categories. Secondly, transportation from the farm to the manufacturing plant contributes a significant impact to ozone depletion, carcinogenics, and non carcinogenics. Looking at the comparison chart of the three processes, coconut husks dominate most categories. In the ozone depletion category, wood has the largest relative impact. In this category for wood, the largest contributors were transportation and the use of diesel fuel. Coconut husks had the largest relative impacts in global warming, smog, acidification, eutrophication, respiratory effects, ecotoxicity, and fossil fuel depletion. Coal had the largest relative impact in the carcinogenic and non-carcinogenic categories. Those impacts come from the mining process itself and not the transport of the material. The major impacts that we see in the comparison figure are due to the methane, carbon monoxide and coal dust emissions during coal mining which have serious health implications for the workers who are exposed to them.

A.4.2 Activation Process Life Cycle Analysis

Activated carbon can be prepared from almost any organic material rich in carbon and small amounts of inorganic matter (3, 10). The activation process is well known (Figure 6). Prior to activation, samples are prepared through pulverization to produce powders of each sample to a diameter near 200um-1mm (Ruiz-Fernandez 2011, Okhovat 2012). These small powders increase the overall surface area available for pyrolysis and carbonization, maximizing the amount of pore space available for adsorption of contaminants. For the purposes of this assessment, the pulverization step was not considered (Figure 6) because it was assumed that all 3 samples could be prepared in the same manner with the same device.

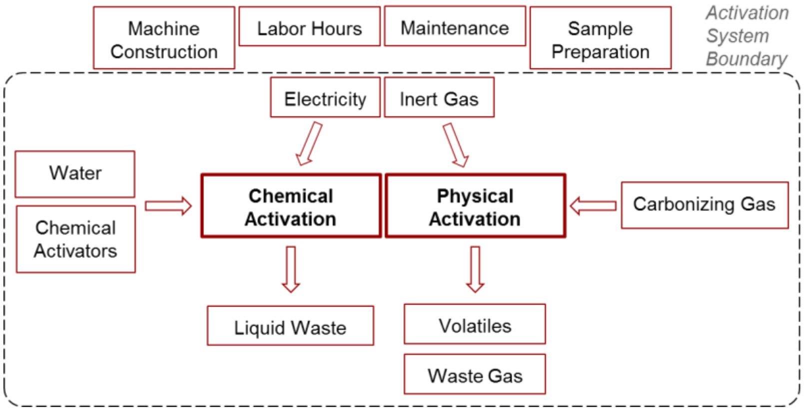


Figure 6. The boundary conditions determined for the physical/chemical activation of GAC.

The two main industrial strategies for preparation are physical (or thermal) and chemical activation (Reuiz-Fernandez 2011). Physical activation occurs at high temperature (700-900C) in which the char from carbonization is partially gasified by an oxidant atmosphere (steam or carbon dioxide) (Ruiz-Fernandez 2011, Okhovat 2012). In chemical activation the precursor is impregnated with a chemical (usually H_3PO_4, however other chemicals can be used for this process including $ZnCl_2$ and Na or K hydroxides or salts), carbonized under an inert atmosphere at lower temperature, and then washed to remove residual chemicals (Ruiz-Fernandez 2011, Okhovat 2012). The main pathway difference between the two is that in physical activation, carbonization and activation are independent steps whereas in chemical activation the chemicals added activate the material as it is being carbonized. Previous literature has shown that physical activation leads to smaller pore sizes and less deviation between poor sizes on average than chemical activation (Ngernyen 2006, Chromalox). Because of this, physical activation should be used in gas storage and gas-filtration applications, or applications that demand a smaller pore size on average. Literature has shown that the pore size obtained from physical activation is dependent on the amount of time that a material has been carbonized and thus with longer activation times larger pore sizes can be achieved (Ngernyen 2006). While chemical activation delivers pore sizes that are more applicable to water filtration, there is concern with using carbon activated in this way due to residual chemicals from the synthesis pathway. Chemical activation processes also have a higher yield (35-50%) on average when compared to physical activation processes (2-30%) (Ruiz-Fernandez 2011, Okhovat 2012, Ngernyen 2006, Chromalox).

Using these boundary conditions, calculations for the energy required for the physical and chemical activation of the samples were performed using the following equation (Brugge 1997),

$$E = V\ \rho\ t\ C_p\ \Delta T$$

Where E is the energy required (kW), V is the volumetric flow rate of the gas (L/min), ρ is the density of the gas used (kg/m_3), t is the time of reaction (min), C_p is the heat capacity of the sample (J/(kgK), and T is the temperature of reaction (K). Heat loss was assumed to be negligible for these calculations. Values were calculated using a flow rate of 100L/min of N2 and 150L/min of CO_2 which was scaled-up from values that were obtained from the literature for this method (Ruiz-Fernandez 2011, Okhovat 2012, Ngernyen 2006, Chromalox), densities of 1.251kg/m_3 of N_2 and 1.98kg/m_3 for CO_2 (Fono-Tamo 2013), specific heat of J/(kgK) for coconut shell (Lee 2013), 1.38 J/(kgK) for coal (Radmanovic 2014) and 1.4 J/(kgK) for wood (Radovic 2017). The energy requirements for heating 110T of each material are calculated and can be found in the supplemental information.

A life cycle assessment was run making additional assumptions using Simapro software (Figure 7). A general activation procedure was determined and used for each material and was determined from a literature review (Reuiz-Fernandez 2011). This procedure included 2 hours of pyrolysis in nitrogen at 750C followed by 8 hours of activation in CO_2 atmosphere at 850C. Based on CHN elemental analysis found in literature, the overall C content of the 3 main source materials was found to be 80% (Ruiz-Fernandez 2011, Meier 2013), 44% (Mazlan 2016) , and 52% (White 1997) for coal, wood, and coconut husk respectively. Yield of activated carbon for physical and chemical activation procedures was assumed to be 50% and 30% respectively. On average, the final yield values are lower than what was found in literature using these assumptions. TRACI 2.1 assessment was used to determine the relative impacts of each material to the overall process.

The results of this assessment show that activated carbon using physical activation is, on average, more environmentally impactful than chemical activation. However, the impact percentages are surprisingly high for wood as compared to coal in several of the impact categories. This is because using physical activation of wood requires a significant amount of energy since there is very low product yield (considering it has the lowest initial carbon content as compared to coconut husks and coal). Further, burning the source materials at high temperature releases volatile components into the atmosphere. Also, more wood needs to be burned on average to compensate for the lower carbon content in the activated carbon which accounts for why the environmental burden is so high. Physical activation of coal is particularly damaging regarding ecotoxicity and non-carcinogenic impact factors. This is largely due to the impact associated with the volatiles that come off when the coal is burned at high temperature during this activation mechanism. Coal compounds also contain a variety of heavy metal and other metallic components (in small amounts) that contribute heavily to the environmental impact of this pathway. Looking comparatively, physical activation tends to have a higher impact on average overall due to the significant energy demand associated with the high temperature demand for this pathway.

Chemical activation is showing the most surprising result in that coal is the least environmentally impactful source material and coconut husk shows the highest impact factor overall. This is because volatiles are not as much of a concern using this pathway, considering the reaction is run at much lower temperature. Further, coal contains the highest carbon content of any of the 3 source materials and one needs to put in significantly less of it to achieve the same amount of activated carbon at the end as compared to wood or coconut husks. Both materials contain nearly half of the original carbon content as coal. Therefore, since there is significantly less waste ash being generated using this source material this could be contributing to the conclusion achieved from analysis.

The quantitative assessment up to this point has suggested that while coconut shells may seem like the most sustainable option, when the full lifecycle of activated carbon is considered the answer is much more complex than it may have seemed. The most sustainable source material is highly dependent upon the activation mechanism, where physical activation on average has a higher environmental impact than chemical activation due to the larger number of volatile compounds and higher energy demand. Burning coal releases a significantly higher concentration of volatile compounds into the environment than the other 2 source materials but has the lowest increase to ozone reduction, global warming, smog, and fossil fuel depletion due to its higher carbon content. Chemical activation has a significantly lower environmental impact overall than physical activation due to the lower energy input, but for this process coal has the lowest environmental impact due to the higher initial carbon content. Therefore, it is the recommendation of the authors - based on the assumptions made in this paper - that industry pursue chemical activation for this material when possible. When using chemical activation, based on the assumptions made in this report, it is advised that industry pursue coal as a source material.

Figure 7. A comparison of the 3 source materials through physical activation, chemical activation, and both in one comparison.

A.4.3 Social Life Cycle Analysis

I. Introduction

Each of the source materials come from a unique social situation within entirely different countries and political systems. Coal mining in China, timber from Venezuela, and coconut farming in Indonesia are drastically different production systems under different state and international regulations. They each, also, have different rates of illegal activity and government oversight. While these differences make the social situations hard to compare, here the authors use both qualitative information and the Simapro Social Hotspot Database to better understand the social impacts and ramifications of sourcing the materials.

First presented is the qualitative information that was retrieved from ethnographic work of other anthropologists, as well as information from state organizations, nonprofit agencies, and international agencies. While this information creates a representation of farming or mining in these countries, it does not create a perfect or complete picture. Recent political changes as well as gaps in these records cannot be fully accounted for. Second, the outputs are presented from the Social Hotspot Database. It also has assumptions and calculations that are limitations. Together though, these two methodologies provide one representation of the social harms that are present in these production systems.

II. Qualitative Literature

Coconut Farming in Indonesia

Coconut farming in Indonesia is typically not large-scale plantation farming. Different contract farming schemes are used to grow and harvest the coconuts for all sectors. Contract farming consists of agreements between local farmers and some centralized organization. Alternatively, they may be a cooperative organization between the farmers to then negotiate with the larger organization. In Indonesia, there was a push towards this form of agroindustry during development projects sponsored by the state and conducted by the World Bank. There was a 20-year cycle set up to manage land leased to farmers and then to re-loan them money as part of the next set of plantings. Some have cited this as a socio-governmental control method, while others note that intercommunity inequality has declined.

Part of the method of control is embedded in the price fixing that occurs around the commercially grown coconut species. The value that raises the price the most, the ‘naturalness’ of the coconut, is embedded long after it has been sold by the farmer. So, the price it’s sold for by the farmer is far less than the ultimate sale price. This leads to the inequality embedded in the contract, even if legally contracts are used to equalize parties.

Invisible labor is especially common in coconut farming. Growing coconut does not provide a living wage. So, someone, typically the man in the household, must work a different job as well. Even though most of the land is owned or leased to men, it is women and children who work on the land. This is especially problematic in cases of divorce when women lose access to the land that they had been working on. State officials have gone as far as to send couples to an Office of Religious Affairs before giving a legal divorce, because of these implications. Falls, machinery accidents, diversion from other farming activities, regional political history, and volatility of the market are also important (Hornby 2010).

Coal Mining in China

There are two main types of mines that have been found in the literature. State-owned large mining oppositions and illegal mines. State-owned mines operate more like small cities than mines. Each has worker lodging, markets, stores, and other businesses. Here, miner safety and regulations are somewhat observed. Even with these rules, mining in China can be deadly. 2,631 deaths in 2009 were reported as being caused by working in the mines. Many more are related to mining activity (Zhang 2007). These included respiratory illness and other, mostly airborne, diseases. Dangerous illegal mining in China is also common. Illegal mines are typically 1 meter across shafts that one person climbs into. This person then hand digs the coal out and it is transported by cart or sometimes a crane (depending on the number of shafts). These types of mines are also at high risk for including forced labor. Because of these risks and political decisions to increase renewable resource use for energy production, there has been an increase in state forces closing illegal mines (Zhang 2007).

China has begun to close illegal mines and recently closed around 1,000. Part of the prompting to close the mines has been the Paris Climate Agreement. The state is also moving away from state-owned mines. The crack-down on illegal mines in China has also changed migration patterns in the region. Anthropologists have noted that migrant workers from Nepal are moving into India to work in coal mines (illegal type mostly) and other mines are opening in Mongolia (Welle 2017).

Forestry Plantations in Venezuela

Much of the anthropological literature focuses on politics and indigenous people rights in Amazonia. There the Amazon Cooperation Treaty has been enacted to stop illegal logging and loss of forest cover. Recent political and economic instability in Venezuela has made it harder to enforce regulation. Similarly, a lack of federal level funds has led to the dissolving of state regulations to protect forests. Still, much of the timber coming out of Venezuela is from forestry plantations (International Tropical Timber Organization 2017). The forestry sector brings $1.4 billion into the country and accounts for 0.5% of the country's total GDP (44). Currently there are an estimated 56,000 people working in the forestry plantations. To the best of our knowledge, little information on the plantation system itself can be found. International standards highlight risks to life and limb, as well as to the continuation of forest cover loss in the region as detrimental to ecosystems (International Tropical Timber Organization 2017).

III. Simapro Social Hotspot Analysis

The Simapro Hotspot Database (Benoît 2009) highlights many of the same concerns that were indicated in a review of qualitative data. Within the social data, there are multiple ways to view the information. The weighted datasets were chosen because they incorporate risk assessments into the calculation of social impacts. Weighting of the different social indicators was done by the experts who compiled the database. They used a combination of risk assessment, qualitative and quantitative information, and subjective judgment to weigh the social indicators. The indicators were grouped into low, medium, high, and very high risk according to the assessment of the experts on how prevalent the impact is in each country (United National Environment Program 2013).

Coconut farming makes up one portion of the plant fiber production sector in Indonesia. These scores need to be broken down based on the percentage of impacts by coconut farming. I calculated an allocation based on data from the Food and Agriculture Organization for the United Nations (FAOSTAT 2017). From this data, the total monetary value of crops in Indonesia was found and then calculated the proportion of value attributed to coconut. That proportion was approximately

3% for 2014, the most recent available data. The total social impact of $100,000 (total) was multiplied by 0.03 to find the approximate social impact of $30,000 (3%) that is attributed to coconuts. It is that proportion of social impact that is represented in following charts or graphs.

In order to have equal measurement units to understand the social impacts of one resource in relation to the other two, $30,000 of value produced was treated as the functional unit. For coal and forestry, which are sectors unto themselves, the unit of measurement in Simapro social database was changed to $30,000. The outputs from Simapro then for all three resources are for the approximate impacts associated with $30,000 of production. It is not the total for coal in China or forestry in Venezuela. The social impacts represented here are in relation to each other and not the total impact of coal mining or forestry in the respective countries.

Represented in is chart is the weighted social impacts for each country for the respective resource (Figures 8 and 9). More specific numerical breakdown of this information can be found in the supplemental information of this work. By looking at the totals here, the source with the highest levels of negative social impacts is coconut with wood second, and coal having the least. The units are represented in labor hours impacted by the production of a set amount of monetary value. The following graphs show the indicators and impact within the top impact category for each country/product, which is labor rights and decent work (red). Second for coconut and coal is health and safety, while the second highest damage category for wood is governance (orange). Damage categories that contribute the third highest impacts are in gold.

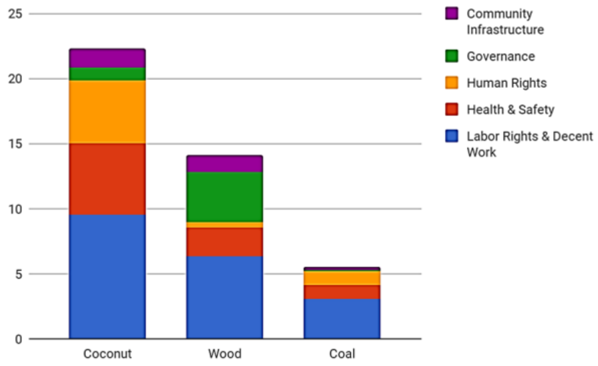


Figure 8. A comparative social lifecycle analysis result for coconut, wood, and coal.

Labor and decent work as a damage category include indicators such as forced labor, excessive working hours, child labor, wages under minimum poverty levels, and lack of freedom to gather or unionize. For each product, the social indicators that contribute the most to the damage categories are different. The following charts show the important social indicators for the three products in the labor rights and decent work category, which is the most impactful category.

IV. Discussion of Social LCA

Although these indicators are vague, paired with qualitative information a representation of what is occurring becomes clearer. For each of the products, the social indicators within the damage category of labor rights and decent work are different. These differences show how different problems within the supply chain can cause harms that are all categorized as issues with labor and working rights.

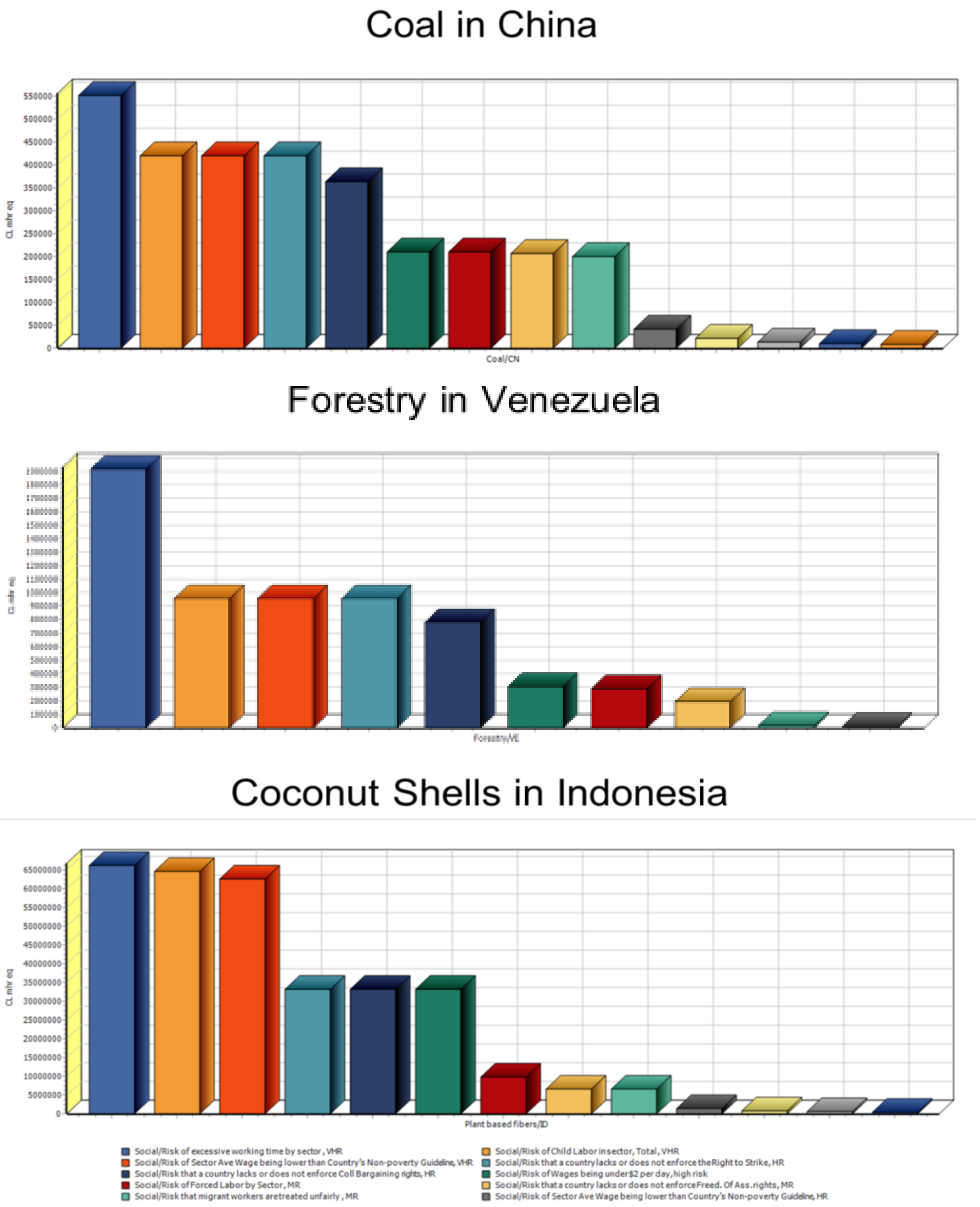
Coal production in China has impacts primarily related to forced labor, migrant labor mistreatment, and workers' rights. Workers' rights include indicators such as rights to associate, gather, or collectively bargain. These indicators affirm concerns in the qualitative data. Both types of mining, legal and illegal, are dangerous with many health and safety hazards. Miners in illegal mines in particular, are faced with long working hours, unsafe conditions, and risks of forced labor. Migrant labor around the region do move throughout the illegal mining industry. In these cases, migrant workers are especially vulnerable to working under forced labor conditions or being mistreated through excessive working hours or poor safety standards.

Forestry in Venezuela, like many sectors in the country, has issues related to workers' rights and pay. The top social indicator here is that wages are below the poverty line and at times below $2 USD a day. Workers' rights and wages begin to touch on issues of governance related to the political instability in Venezuela. Recent news reporting highlights the continuing instability (Semple 2017). Debt default remains a real risk and continued United States sanctions continue to be cited as a source of instability within the financial sectors. Without the funds to enforce legislation on conservation, there has been an increase in illegal logging within the Amazon forest. These financial concerns are present in reporting and in the hotspot database through low wages and high impacts related to governance.

In Indonesia within plant-based fibers sector, there are different social indicators present. Here, excessive working time and child labor are two of the top concerns. Again, these are reflected in the qualitative data from ethnographic sources. Coconut is produced on contract farms where the profit from growing the coconut is not a living wage. As discussed above, men typically leave the home in order to work, while women and children work farming coconut. The invisible labor of children is a central concern within the hotspot database.

The social indicators within the labor rights and decent work category are different for each of the products. The relevant social indicators represent the different social and political concerns present in the different countries. The qualitative data from ethnographies, news reporting, and non-governmental agencies show how these social indicators represent real concerns and risks that individuals working in the production of these products face. Combining the qualitative and quantitative data creates a clearer representation of what the social indicators mean in context and in people's' lives.

In addition to high risks associated with labor and decent work, there are many indicators that are shared between the cases regarding health and safety and other categories. In forestry and coal mining in particular, there is an increased risk of respiratory problems resulting from inhaling carcinogenic materials, as indicated by the hotspot dataset. Risk of fatal injury is present in all three cases.



Coal in China

Forestry in Venezuela

Coconut Shells in Indonesia

Figure 9. A breakdown of the 3 source materials for their social impacts.

V. Assumptions & Limitations

Limited access to qualitative data was a problem, especially regarding information from Venezuela. Language and translating information from Spanish into English was an option but was time consuming and increased the chance of major errors or assumptions being made. Limitations of data also exist due to limited ethnographic research being done at the different sites recently. While ethnographic work has been done in all three countries, at times the information is dated. Currently, ethnographic work needs to be done to find how local production of these materials has changed over time.

Calculations rely on linear correlation between economic value and social impacts/harm. The underlying economic model does not capture the true amount of harms that may be attributed to sector. Capturing the true amount of harm is not currently possible based upon access to information and the interrelatedness of social structures. In addition, the model assumes a linear connection between the monetary value and the impact. This assumption is highly suspicious. While the economic scaling is necessary to quantify the results, there is no proof that a linear correlation exists. For production, the harm may be heaviest beginning the process and then not increase as dramatically as economic value increases. Without further research into the relationships between economic value and social impact, there is no way to know. As a result of the assumption of linearity and the ambiguous measurement units, it was found to be more reasonable to look at the proportions between the resources comparatively.

Within any production system there are many stakeholders and perspectives. Within this report one representation of each of the processes has been shown. This representation is corroborated by the hotspot database and is reasonable but is still only one representation. Within this representation only the negative social impacts have been shown. Currently there is not a method through which to represent any benefits that may be attributed to the resource production.

Scale of analysis is particularly important to understanding the limitations of these results. Qualitative data is most commonly looking at a local, community, or providence scale and recording the lived experiences of those people. The hotspot database, on the other hand, is calculating risk per sector at the national level. Putting information from these two scales together within this analysis was very productive to understand the situation.

VI. Conclusions of Social Analysis

This analysis shows that all three sources for activated carbon have serious negative social impacts. The qualitative information alongside the Social Hotspot data indicate that these are production systems that take advantage of vulnerable populations, participate in the use of child labor, and have high risks of fatal injuries. Marketing of one source, such as coconut shells, as more natural and so sustainable is more than misleading. It is false. None of these products provide a socially sustainable source for activated carbon, and coconut shells may be worse than the others.

A central variable in the analysis is scale. The qualitative information highlights how the production process impacts the lives of miners and farmers in different ways within varying contexts. Taking this scale into account, it becomes clear that all three sources have serious and harmful social impacts. Simapro Social Hotspot data operates at a national/state level. The data here is quantified and does not contain the same narrative, ground level information. Instead, it takes that information and ascribes risks based on known working conditions. The varying scales both enhance and complicate the analysis.

Using qualitative and quantitative data together provides a clearer representation of the social impacts associated with production of these three resources. This analysis adds to the environmental LCA of activated carbon and contributes to a more holistic LCA, which addresses both environmental and social elements of sustainability. Together the environmental and social LCA provide a good representation of the harm that is created through the resource acquisition and processing into activated carbon.

A.5 Conclusions of Assessments

Sourcing, process, and social life cycle analysis indicate that the definition of sustainability in this application is much more complicated than was initially suggested by industry. While coconut husks may seem to be the most sustainable option on the surface, when one considers the full spectrum of sustainability - economic, environmental, and social sustainability included - the answer becomes more complicated. Sourcing-driven analysis indicated that comparatively speaking the coconut husks had the highest environmental impact. Process-driven analysis showed that for physical activation coal seemed to have the largest impact in specific categories (ecotoxity) due to the presence of contaminant metals in the coal and volatiles released during the high temperature activation step while wood and coconut had the largest impact for the other categories that were considered for this analysis. This indicated that no source material was significantly worse than any other, but each had their own impacts on the environment. However, chemical activation proved the most surprising in that the coal sourced activated carbon seemed to have the least environmental impact since this synthesis is run at comparably lower temperature for less time and the fact that coal has a much higher carbon content than wood or coconut husk. Social – driven analysis indicated that all the materials have serious negative social impacts overall. Concerns about vulnerable populations, child labor, and high risks of fatal injuries for all 3 souring materials indicated that there is significant room for improvement in this area.

It is the hope of the authors that this information will be used to help industry develop more appropriate definitions of sustainability. Sustainability is much more than choosing a source material that is biologically derived – it demands a full analysis of the material including social, economic, and environmental impacts. Limitations in this work came mostly from the lack of available information from industry. Industry should use this analysis to help develop a more appropriate life cycle analysis for these source materials to choose the most sustainable one overall for their application. Industry is challenged to communicate further down the supply chain to determine the working conditions for workers on farms to determine whether the process is truly sustainable.

A.6 Suggestions

The analysis for this report indicates that specific areas of the manufacturing process for each method can be improved to help minimize the environmental impact of the systems. Many of the environmental impacts are not related to and inhere to the material itself, but the manufacturing processes themselves. In the area of coal mining, the use of better boilers can minimize the impact of this route. For logging, using better and less-environmentally impactful equipment for the extraction tractor and transport truck can minimize the impact. Using less-impactful fertilizer for coconut growing can also help minimize impacts.

A.7 Acknowledgements

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A.8 Bibliography

Activated Carbon Petition, USDA Organic Materials Review petition, Canadaigua Wine, May 2002

Activated Charcoal Review Sheet, USDA Organic Materials Review, February 2002.

Ahmadpour A, Do D. “The preparation of active carbons from coal by chemical and physical activation” Carbon 34(4). 471-479, 1996.

Arena, Noemi. Et. al. (2016 July 1). “Life Cycle Assessment of Activated Carbon Production from Coconut Shells.” Journal of Cleaner Production, 125.

Aura Marina Hernandez, Mary Labady, Jorge Laine. (2014). Granular Activated Carbon from Wood Originated from Tropical Virgin Forest. Open Journal of Forestry, 4, 208-211.

Ben White (1997) Agroindustry and contract farmers in upland West Java, The Journal of Peasant Studies, 24:3, 100-136, DOI: 10.1080/03066159708438644.

Benoît, C.; Mazijn, B. Guidelines for Social Life Cycle Assessment of Products; UNEP/SETAC Life Cycle Initiative, Sustainable Product and Consumption Branch: Paris, France, 2009.

Bourke, Marta "Activated Carbon for Mercury Removal". (1989).

Bruckman, Viktor; Varol, Esin Apaydin; Uzun, Basak; Liu, Jay, eds. Biochar: A Regional Supply Chain Approach in View of Climate Change Mitigation. Cambridge, UK: Cambridge University (2017) Press. p. 46-69.

Brugge HB, Holste JC, Hall KR. “Densities of carbon dioxide + nitrogen from 225 K to 450 K at pressures up to 70MPa.” Journal of Chemical Engineering Data (1997) 42: 903-907.

Chromalox “Technical information: Determining energy requirements – air & gas heating.” Chromalox Technical Documents. I-16-I-22.

Deutsche Welle. “China Coal Consumption Declines for Third Straight Year (2017) www.dw.com/en/china-coal-consumption-declines-for-third-straight-year/a-37755092.

Dillon EC., Watson WA., et al. “Large surface area activated charcoal and the inhibition of aspirin adsorption.” Annals of Emergency Medicine. 18(5). 1989. 547-552.

EPA Alumni Association: Senior EPA officials discuss early implementation of the Safe Drinking Water Act of 1974, Video, Transcript (see pages 15-16).

EPA. “Water Health Series: Filtration Facts.” 2005. Pp. 1-10

FAOSTAT “Food and Agriculture Organization of the United Nations.” (2017), www.fao.org/faostat/en/#data/QC.

Fono-Tamo RS, Koya OA. “Characterization of pulverized palm kernel shell for sustainable waste diversification.” International Journal of Scientific & Engineering Research (2013) 4(4): 6-10.

Global Forest Watch: Venezuela. http://www.globalforestwatch.org/country/VEN

Hernández, A.M., et al. (2014). Granular Activated Carbon from Wood Originated from Tropical Virgin Forest. Open Journal of Forestry, 4, 208-211. http://dx.doi.org/10.4236/ojf.2014.43027

Hernández, G. (2017, October 02). Madera Ecológica, Una Opción Sustentable para Venezuela. Retrieved December 07, 2017, from http://si-venezuela.com/madera-ecologica-una-opcion-sustentable-venezuela/

Hornby;, Lucy. “China Reports Fewer Coal Mine Deaths in 2009.” Reuters, Thomson Reuters, 14 Feb. 2010, uk.reuters.com/article/china-coal-deaths/china-reports-fewer-coal-mine-deaths-in-2009-idUKTOE61D00V20100214.

International Tropical Timber Organization (ITTO): Venezuela. (2005) http://www.itto.int/sfm_detail/id=12590000

J.G. Woodruff. “Coconuts: Production, Processing, Products.” AVI Pub. Co. Second ed. 1979.

Laschi, Andrea, Marchi, Enrico, Gonzalez-Garcia, Sara. (2016, April 22). Forest Operations in Coppice: Environmental Assessment of Two Different Logging Methods. Science of the Total Environment 562. http://dx.doi.org/10.1016/j.scitotenv.2016.04.0410048-9697/

Lee AL. “Heat Capacity of Coal.” Institute of Gas Technology.

M.K.B. Gratuito, T. Panyathanmaporn et.al. (2008). Production of activated carbon from coconut shell: Optimization using response surface methodology. Bioresource Technology 99, 4887-4895.

Mazlan MAF, Uemura Y, Yusup S, Elhassan F, Uddin A, Hiwada A, Demiya M. “Activated carbon from rubber wood sawdust by carbon dioxide activation.” (2016) 148: 530-537.

Meier S, Rector LR, Allen G, Hopke P, Chandrasekaran SR, Lin, L. “Elemental Analysis of Wood Fuels.” New York State Energy Research and Development Authority. (2013).

Miranda, Marta, et al. (1998). All that Glitters is Not Gold: Balancing Conservation and Development in Venezuela’s Frontier Forests. Washington, DC: World Resource Institute, Forest Frontiers Initiative.

Ngernyen Y, Tangsathitkulchai C, Tangsathitkulchai M. “Porous properties of activated carbon produced from Eucalyptus and Wattle wood by carbon dioxide activation.” Korean Journal of Chemical Engineering (2006) 23(6): 1046-1054.

Noemi Arena, Jacquetta Lee, Roland Clift. (2016). Life Cycle Assessment of activated carbon production from coconut shells. Journal of Cleaner Production, 125, 68-77.

Okhovat A, Ahmadpour A, Ahmadpour F, Yadegar ZK. "Pore size distribution analysis of coal-based activeated carbons: investigating the effects of activating agent and chemical ratio." International Scholarly Research Network Chemical Engineering. (2012). 1-9.

Platts "China to Cut Coal Mining Capacity of SASAC-Owned Companies by 10% in 2 Years." (2016), www.platts.com/latest-news/coal/hunan-china/china-to-cut-coal-mining-capacity-of-sasac-owned-27622480.

Radmanovic K, Dukic I, Pervan S. "Specific heat capacity of wood." Drvna Industrija (2014) 65(2) 151-157.

Radovic L. "Chapter 7: Coal" The Science of Activated Carbon https://www.ems.psu.edu/~radovic/Chapter7.pdf. Web. (Accessed: 12/1/17)

Ruiz-Fernandez M, Alexandre-Franco M, Fernandez-Gonzalez C, Gomez-Serrano V. "Development of activated carbon from vine shoots by physical and chemical activation methods. Some insight into activation mechanisms." Adsorption (2011) 17: 621-629 DOI 10.1007/s10450-011-9347-1.

Semple, Kirk, and Clifford Krauss. "As a Debt Deadline Looms for Venezuela, Maduro Is Defiant." The New York Times, The New York Times, 2 Nov. 2017, www.nytimes.com/2017/11/02/world/americas/venezuela-debt.html. https://nyti.ms/2iV9UpI

S-LCA methodological sheets. 2013. United Nations Environment Programme and SETAC. https://www.lifecycleinitiative.org/wp-content/uploads/2013/11/S-LCA_methodological_sheets_11.11.13.pdf,

Spencer. "Activated Carbon | Properties of GAC" Accessed: 10/24/2017.

The Freedonia Group ."World Activated Carbon - Industry Study with Forecasts for 2014 and 2019." (2010) 1-379.

Transparency Market Research, (2016, May 02). Global Industry Analysis, Size, Share, Growth, Trends and Forecast 2016-2024. PR Newswire. Retrieved December 07, 2017, from https://www.prnewswire.com/news-releases/wood-activated-carbon-market-expected-to-reach-us-4560-mn-in-2024---global-industry-analysis-size-share-growth-trends-and-forecast-2016---2024-tmr-577799541.html

Waney, Nordi F.L. et. a. (2002). "Traditional versus Intensive Coconut Farming in North Sulawesi." Sam Ratulangi University, Department of Agriculture.

Zhang, Junfeng (Jim), and Kirk R. Smith. "Household Air Pollution from Coal and Biomass Fuels in China: Measurements, Health Impacts, and Interventions." Environmental Health Perspectives, National Institute of Environmental Health Sciences, June 2007, www.ncbi.nlm.nih.gov/pmc/articles/PMC1892127/.

APPENDIX B. THE CORPORATE EQUALIY INDEX IS A METHOD OF ENABLING HETERONORMATIVE CULTURES TO PERSIST IN SCIENCE

For this work I am the sole author. I performed the entire analysis by myself and was inspired by my experiences to write this. This work is currently under review in the *Harvard Business Review*.

B.1 Abstract

Although it is estimated that 2.5-3.5% of the population – and consequentially 5-8 million employees – in the United States identify as a gender and/or sexual minority (GSM), there is a significant lack of protective legislation at the federal and many state levels. This confusing landscape can be quite daunting for a GSM employee, and the Human Rights Campaign has developed the Corporate Equality Index (CEI) to help potential employees understand how GSM-friendly a company is. While this measurement tool is widely accepted and suggested throughout the science, technology, engineering, and mathematics (STEM) disciplines, more recent literature has found significant weaknesses in the ratings system leading some to question the reliability and accuracy of the tool overall. In this work, the CEI is further critiques for its inability to measure the individual experience of an employee engaging with office and local cultures at a which were identified through the lens of a personal internship experience. Through a literature review, strategies for combating this weakness in the system are determined. An explanation is provided for the reasons behind the complexities of this situation as it pertains to STEM cultural frameworks. Conclusions from this work show that without significant effort from the upper-management to change institutional cultures, negative cultures will persist. Further, this work shows that not only institutional cultures but local policies in which the individual offices are located can have monumental impacts on employee retention and satisfaction. The metrics used by the CEI to measure GSM-friendliness of a company are flawed in their current state and must be altered to include the company's commitment to changing local and office cultures to also account for the ways that companies challenge the pervasive heteronormative and apolitical cultures that exist in the STEM fields. Without such alterations to this system, companies who strive only to achieve a 100% on the CEI will not maximize GSM worker productivity, satisfaction, and job retention.

B.2 Introduction

It is estimated that 2.5-3.5% of the population of the United States is lesbian, gay, bisexual, and/or transgender (LGBTQ+) and that this population represents nearly 5-8 million of all employees across the United States. (Johnston and Malina 2008, Gates 2013, Pizer et al. 2012) While it is possible for some people in this community to hide their sexual orientation or gender identity in the workplace, many people within this community physically wear their identity at work, such as people mid-transition and people who identify outside of the gender binary. Surprisingly, there are currently no federal statutes addressing employment discrimination based on sexual orientation or gender identity in the United States, making it legal to discriminate and terminate employees based on their sexual orientation and gender identity alone in many US states. (Johnston and Malina 2008, Wang and Schwarz 2010) Many companies have now added sexual orientation and gender identity to their non-discrimination policies to help combat this, but many others have not, and keeping track of the individual policies for each company, state, and country in which one works can be a significant challenge. For this reason, it is now more important than ever for gender and sexual minority (GSM) engineers and their allies to be cognizant of the rights of GSM individuals when entering a new job or hiring a new employee – especially when that job requires relocation to a different state or region of the United States.

To address this problem in the United States, the Human Rights Campaign (HRC) – a national organization that serves to help protect and advocate for the GSM community – has put together a complex scoring system for companies to measure how GSM-friendly they are, and has published the results online. This system is referred to as the corporate equality index (CEI) in the United States, although there are other systems throughout the world including Stonewall Workplace Equality Index in the United Kingdom. (Human Rights Campaign 2015, Godwin 2013) Companies score “points” by providing resources listed on their website to GSM employees, including having protections against termination based on gender identity or sexual orientation, having an employee resource group (ERG) for GSM employees, providing domestic partner benefits, covering gender reassignment surgery, and many others. Points are assigned to specific metrics and are described in depth within the annual report (Table 1), where the maximum score is 100%. In order to get rated, companies simply need to have 500 full-time US employees and to contact the HRC – and participation is free. Many scores are given based simply on what is available on a company website, and not based on actual data provided willingly by the company. These scores are designated in the report by being colored in a lighter gray color as opposed to the black scoring for companies that opted into the system. While the CEI is to be celebrated for its ability to push large companies into providing GSM-friendly benefits, as over 600 companies have received a perfect score by this rating system, it has been criticized more recently for a variety of reasons.

Table 1: The scoring system of the CEI as listed in their annual report

Point Value	Provided Benefit
15	Prohibits discrimination based on sexual orientation for all operations
15	Prohibits discrimination based on gender identity or expression for all operations
5	Has contractor/vendor non-discrimination standards that include sexual orientation and gender identity
10	Offers equivalent spousal and partner medical benefits
10	Parity across spousal and partner “soft” benefits
10	Offers transgender-inclusive health insurance coverage
10	Firm-wide organizational competency programs
10	Has employer-supported employee resource group or firm-wide diversity council
15	Positively engages the external LGBTQ community

The first major criticism of the CEI is that the maximum score a company can get is 100%, and once a company obtains a 100% rating, there is no benefit to providing additional services to GSM employees unless the scores and requirements change. Companies are encouraged through this system to simply meet the minimum requirements to achieve a 100% in the report and are not incentivized to offer additional benefits to its GSM employees. The second major criticism of this scoring system is that the scaling of points unfairly leaves behind people who identify as transgender, genderqueer, gender non-binary, and agender. As it currently stands, it is possible for a company to get a perfect score without covering gender reassignment surgery or having employee access to a single gender neutral bathroom. (Human Rights Campaign 2018) To combat some of the above criticisms, for their upcoming 2019 CEI report businesses must offer coverage available to domestic partners of employees and remove transgender exclusions from all benefits plans in order to achieve a 100% rating, therefore showing that they are willing to combat these criticisms of the system as a whole. (Human Rights Campaign 2018) HRC’s commitment to making the system better is shown by these incremental adjustments, but is still currently flawed by lacking requirements that benefit transgender, genderqueer, gender non-binary, and agender people.

While these criticisms are valid and valueble, I propose, herein, an additional outlet of critique of the CEI. This criticism is based on personal experience this past summer at an internship I had at a company that received a 100% on the CEI, despite being located in a state and city that does not have legal protections for GSM employees. While the CEI ratings system is strong in many aspects, this rating system does a poor job of reflecting what a GSM engineering employee encounters on the day-to-day, even at a company with an ERG that boasts its CEI rating and that recruits at national GSM-themed conventions. In particular, the CEI rating does not account for the variations in GSM-friendliness between offices in different locations within the same company. This rating does not account for personal interactions that GSM employees have at work with their supervisor or their co-workers, who may or may not be allies. This problem is exacerbated at companies that operate worldwide where an employee may get a promotion or new job that requires them to travel from a GSM-friendly environment to an unfriendly one, even when the company has a perfect CEI rating worldwide.

B.3 My Experience in Industry

Before starting my internship I did my research. As a gay-identifying graduate student, I applied and specifically looked for internships at companies that scored 100% on the CEI. I looked for this metric in companies because my GSM mentors in the field suggested it as a facile way to identify GSM-friendly companies. I stumbled upon a unique internship at a large engineering firm that would provide me with a valuable research project, adding a new skill to my resume before I graduated from graduate school. This opportunity seemed like a no brainer – I would intern at a company that appears to offer a safe space for its GSM employees while providing an enriching research experience.

During the interview process, the GSM components of my resume never came up. I was actively involved in numerous GSM-themed organizations, but I was not asked questions about these activities during my interview. I was shocked because these activities are where my passions lies, and it is where I believe I truly excel. My interviewers focused on the more technical aspects of my resume including my thesis work and my publications and carefully stepped around these more diverse aspects of my document. The interviewers' silence concerning my GSM advocacy work spoke volumes on their stance about inclusivity prior to me even arriving. I spoke about this to numerous colleagues after the interview, and found that this was actually a common experience among those who were GSM-identified. A few weeks later, I was offered an internship opportunity by the team, and I proceeded to move my life out to a new town in a new state.

I have previously been bullied and harassed for being gay during my undergraduate studies, in graduate school and at the places at which I have worked previously. Because of this, from day one I was anxious in every meeting with my supervisor. I was worried that they would ask me questions about my personal life – and if they did… would I tell them the truth or would I have to lie? The company boasted that it would protect its employees from discrimination, but when it was my word over my supervisor's (who had been in the company for 30+ years), who would they believe? Could I count on the Human Resources manager to be GSM-friendly and investigate my claim without bias or would their opinions cloud their judgment of the situation? How "out" am I allowed to be? These questions haunted me and kept me on edge in every meeting that we had, and prevented me from bringing my full self to my work. I would be working with the equipment in the lab wondering what they would do if they found out – would they retaliate?

As a result, I reached out to multiple people in my professional network, including the head of the company's GSM-related ERG, as well as my colleagues from national GSM organizations, and no one was able to provide the guidance that I needed to persist in a seemingly unsafe space. The most common reply that I got was, "use your best judgment." I realized that having a solid group of mentors in the industry, even having them within your company, is not enough when you enter a new space as an employee. In a hierarchical space where you are far from the top, having a multitude of support systems outside of your management is not enough to make you feel protected and valued. I thought I had done my homework and prepared myself for my first foray into industry, but I realized if I could not be my full self with my supervisor then I could not be my full self in the workplace or in the lab.

I also realized that no one on my team nor a single member of the GSM ERG had been safe-zone trained. My supervisor had certainly not had GSM sensitivity training, and if they had it had not provided them the resources necessary to mentor me. I had witnessed numerous instances of harassment in the workplace and did not speak up for fear of being outed to my team. Because I did not know or trust the people in Human Resources, I did not feel comfortable reporting the incidents that I saw. I realized I had entered a heteronormative space when numerous coworkers asked me my opinions of women without ever asking me if I was straight beforehand. There were very few "safe zone" stickers around my office building (I counted one sticker in total out of the hundreds of offices) – and no one on my team displayed any in their offices. Sure – the company was providing same-sex benefits to its employees, but what was it doing to improve the basic work experience of its entry-level or non-management GSM employees?

B.4 Opportunities for Further Development

Even with the widespread adoption of the CEI system for determining how GSM-friendly a company is, more than 60% of GSM members of the American Physical Society reported being harassed in the workplace, and 40% considered leaving their job in the last year. (Atherton et al. 2016, Feder 2015) Astonishingly, 49% of all transgender participants in this survey reported harassment in the workplace. (Atherton et al. 2016, Feder 2015) A recent survey also showed that 56% of all LGBT workers reported being bullied repeatedly at their job with 72% of them not reporting their bullying to Human Resources. (Nauen 2017)

Research shows that GSM individuals have higher overall job satisfaction and lowered anxiety levels when they disclose their GSM identities at work. (Griffith 2002) But in order to do so, they must expect that their workplace is physically and emotionally safe to come out. (Yoder 2016) However, more recent research shows that even without experiencing direct hostility or discrimination, GSM individuals still feel unsafe in work environments that are dominated by assumptions that suggest that everyone in the workplace is straight and/or cisgendered. (Yoder 2016) In other words, it is simply the notion that GSM employees are the "other" in a space that can create this feeling. This feeling is pervasive and unchanging in STEM in particular because this field emphasizes technical competence and a separation of professional and personal lives, creating a space in which GSM individuals do not feel comfortable discussing personal details in their workplaces. (Faulkner 2009a, b)

With the widespread adoption of the CEI system in STEM, and the consequential, high-level organizational changes that have been made to introduce higher levels of physical and psychological safety of GSM employees in the workplace, why do we still have pervasive issues when it comes to GSM inclusion in our industry – especially at the individual level? With more and more companies receiving a 100% CEI score and introducing company-wide changes to the system/environment, wouldn't one expect less and less people to be experiencing bullying, harassment, and discrimination? How is it possible for a company to provide the necessary steps to getting a perfect score on the CEI, but still have GSM people witnessing, being harassed, and bullied in the workplace?

Herein lies a major limitation of the CEI system. Giving ratings out at the company level completely erases the experience of the individual at an individual office or department within the company. It is just simply impossible to find out what the individual is experiencing when only company-wide initiatives and policies are introduced to increase the GSM inclusivity on a company-wide level. Finding ways to combat the heteronormative environments and cultures in the STEM workplace is critical to increasing perceived comfort levels at the individual company. Introducing company-wide policies in the way the CEI ratings system encourages companies to do does not immediately or even directly cause cultural changes within an office. Changing cultures within a company involves significantly more effort than simply adopting global company policies into a company handbook or changing which insurance provider with which your company works. The CEI system does not account for this in its current state.

Proven Methods of Changing Institutional Cultures

Research shows that instituting positive cultural changes within major corporations is extremely difficult, but a major strategic asset. (Flamholtz 2011, Flamholtz and Randle 2012) There are many ways that institutions initiate cultural change, most often with the aim of increasing worker productivity. There is extensive research into the strategies that can increase the overall adoption of the changes into the offices throughout the company. Such strategies mainly revolve around increasing communication between lower-/mid-level management with high-level management during the development process, as this has been found to drive the vast majority of cultural changes that are widely-adopted within major corporations. (Dulek 2015)

Literature has shown strong links between successful adoption of changes in company cultures and communication. (Frahm and Brown 2007, Kotter 1995, Walker 2007, Westover 2010) The purpose and details of changes not only need to be articulated clearly to employees, but when employees have a perceived voice in developing the strategy and the culture that the organization is intending to pursue, they are far more likely to adopt it. (Dulek 2015) Additionally, purposefully giving lower- and middle-level management a voice in developing a new cultural attitude is essential to getting the individual employee to adopt it. (Dunford and Jones 2000, Kjellberg and Andersson 2003)

Affirmation and commitment from the CEO and upper-management within a company is also a critical ingredient to the local adoption of cultural changes within an organization. The presence and participation of high-level officials in communication is essential – both from an authoritative and symbolic perspective – as it creates a space where employees know that their individual voice is being heard by those at the top. (Dulek 2015, Lewis 1999, Pfeffer 2010) One example of this strategy being employed is if the CEO of the company sends out weekly summaries of the discussions being had about changing the institutional culture to those participating in the discussion. This is a simple method to let people know that the person and/or people at the top are listening, paying attention, and that their viewpoints are important and valued.

However, the most important factor for instituting cultural change within a company is adding to its "story set." (Brown and NetLibrary 2005, Deal 1982, Gottschall 2013, Peters 1984) When employees are trying to identify that a negative company culture exists, sharing individual stories of their experience is the most successful method of identifying that claim. This is because an organization's culture and its stories are intimately linked. In these discussions, stories often emerge as the main form of substance to what individuals experience as the work culture – which is likely to be perceived differently between different individuals. Further, when identifying that a negative culture exists, employees will often use the stories of their personal experiences to provide proof to what otherwise might risk seeming to be an unsubstantiated claim. (Dulek 2015) Stories can provide not only proof of the current cultural climate within an organization to those who might be unaware of it, but can also provide justification for the need to move forward and adopt new cultures or even to maintain the current cultures. (Dulek 2015, Peters 1984) Companies that provide spaces in which employees feel comfortable adding to the story set have significantly increased likelihood of adopting positive cultural changes. (Dulek 2015)

In this way, companies that adopt policies in order to achieve a 100% on the CEI without putting forth significant effort to alter the culture of the individual office are not adopting cultural changes into their business model and will not be successful if they endeavor to be GSM-friendly. Encouraging companies simply to apply for the CEI rating without expecting an additional commitment to cultural change is a proven unsuccessful strategy to improve GSM inclusion. A major limitation of the CEI is that it does not account for a company's commitment to be GSM friendly, and unsurprisingly without it there will be no progress to maximize GSM employee productivity and inclusion.

This major limitation of the CEI system indicates that the system itself is not accurately providing a quantitative representation of the GSM-friendliness of a company to potential employees prior to the hiring process. Simply rating companies based on the global resources that they provide to their GSM employees does not change the individual experiences that one has or will expect to have locally without broader cultural changes. Because of this, there is a clear need for an augmented system that not only accounts for the resources provided, but also accounts for a company's efforts to change institutional cultures. Such a system does not exist at this time, but needs to be developed.

Adjustments to Local Climate Outside of Office to Retain GSM Employees

The happiness of individuals in their current job is not only dependent upon their company's efforts to change cultures at the individual office level. Research shows that location also impacts an individual's job satisfaction level, and moving from one environment to another can significantly impact a worker's job satisfaction level. (Martinson and Wilkening 1984, Fossum 1974, Turner 1965) Factors including identification with political climate, sense of belonging, and others can really impact one's happiness in their environment outside of work. Imagine a transgender individual getting a promotion and having to weigh whether to move to a city in a state with legislation which forbids them from using the bathroom that aligns with their gender identity, or an individual moving to a new location and getting harassed on the street with their spouse.

It is clear that companies which put forth significant efforts to change corporate cultures, but do not put forth efforts to change the culture in the locations where they have offices will not maintain worker happiness and will thus have marked decreases in GSM worker retention. The CEI currently measures whether companies implement internal requirements prohibiting philanthropic giving to non-religious organizations which have a written policy of discrimination on the bases of sexual orientation or gender identity. These organizations can have tangible effects on the local environments in which companies have offices, and this metric can have impacts at local levels which should not be accounted for. However, an ideal ratings system would also measure whether companies operate in localities which do or do not provide:

Non-discrimination policies in housing and healthcare, something currently not accounted for in the CEI but is legally inconsistent throughout the United States.

27% of transgender individuals report housing discrimination, 19% of GSM individuals reported having been refused a home or apartment, and 11% reported being evicted because of their gender identity/expression, although 20 US states, and over 200 cities, towns, and counties have laws prohibiting housing discrimination against GSM individuals. (Bradford et al. 2013, Trasvina 2011) A recent study showed that 12% of transgendered individuals were refused routine healthcare, and 14% reported difficulty getting emergency health care because of their gender identity. (Bradford et al. 2013) Companies which do not make efforts to change these values cannot be truly invested in the happiness of their employees at the individual office. Companies which advocate for legislation in this area can greatly increase the happiness of the individual GSM employee and have higher job retention and satisfaction rates.

Hate crime laws inclusive to sexual orientation and gender identity, something currently not accounted for in the CEI but is legally inconsistent throughout the United States.

Forms of violence against GSM people occur because of prejudice and discrimination against GSM individuals, and happen at a higher rate than they do to non-GSM individuals. (Meyer 2015) Violence against non-cis gendered individuals occurs at a higher rate than sexual minority individuals, and rates of violence against non-white, gay men occurs at a higher rate than white, gay men. (Meyer 2015) In 32 US States, it is currently not prosecutable as a hate crime when this violence takes place based on gender identity or sexual orientation alone, something that often weighs in a GSM individual's decision to accept a new job or whether to stay in their current position. Companies which operate in these states should have a vested interest in changing these policies for the sake of employee retention and happiness alone.

Laws which prohibit discrimination against GSM individuals based on religious belief, such as the Religious Freedom Restoration Act (RFRA), which call for scrutiny of any government action which would substantially burden a person's exercise of religion, without also having legal protections against discrimination based on GSM identity.

Following the Supreme Court's decision in Burwell v. Hobby Lobby, the consequences of state-level adoption of RFRA bills to the GSM population, among others, have become clearer. The consequences of this ruling on GSM individuals is that it granted the right of personhood to businesses, which in combination with states with this legislation but without legal GSM protections, allows for businesses to turn away and legally discriminate against GSM individuals based on religious belief. (Lay 2016) This means that employees of a company with a 100% on the CEI can be employed by this company but be denied service at a restaurant when they are eating in a location they moved to as a result of a promotion by said company. Companies, such as Angie's List and the National Collegiate Athletic Association (NCAA), have already made significant efforts to push back against legislation which would otherwise have this effect on its employees.(Kaveny 2015) These actions by companies should be accounted for in a metric which measures a company's commitment to retaining GSM employees, and the CEI does not in its current state.

Laws which prohibit teachers from discussing GSM issues at school as well as anti-bullying laws which protect children from being bullied based on sexual orientation or gender identity.

Parents of GSM youth must consider their children's safety as well as their own. Because of their sexual or gender identity, GSM youth in the United States are nearly 3 times as likely to have been threatened or injured with a weapon at school and nearly 4 times as likely to skip school because they felt unsafe. (Victoria Scanlan 2001) GSM youth are 2-3 times more likely to attempt suicide and are more likely to become homeless and to be involved in child welfare than their non-GSM counterparts.(Van Leeuwen et al. 2005, Garofalo et al. 1999) One must consider the situation in which a company has made great effort to change the culture of the individual office environment, but has made no change to the experiences of GSM children of employees. These concerns are considered by parents of GSM individuals, and often weigh into their decision to stay or leave a company. Businesses which operate in these states should put forth effort to prevent this legislation from existing for the sake of employee job retention and satisfaction.

B.5 Conclusions

Working as a GSM individual in the US is a quite complicated experience, as the legal protections provided depend on the state/region in which one resides. To address this, the HRC has instituted the CEI rating system. However, the CEI scoring system by itself is not accurately informing GSM employees of which companies are GSM-friendly prior to the hiring process. Simply encouraging companies through a scoring system to provide particular resources to their GSM employees at a company-wide level doesn't change the individual experiences that one has or will have without broader cultural change within the company. Further, it does nothing to help change the heteronormative and depoliticized cultures in STEM which receive continued affirmation through the pervasive and complex cultural systems that exist in our field.

Instituting cultural change involves significant effort in communication at all management levels and providing spaces to alter the broader "story set" of a company. Finding ways to identify and quantify the way that companies not only adopt the broader logistical changes for its benefits to employees, but also how committed they are to changing institutional cultures is a significantly better way to measure the GSM-friendliness of a company. However, changing cultures at an individual office is not enough to truly improve worker happiness. Companies must also encourage localities in which their offices are located to be more GSM-inclusive to maintain GSM worker productivity. These ideas are currently not accounted for in the metrics used by the CEI, and without them companies will have little lasting effects on GSM worker retention. Pursuing these options for amending the way that GSM-friendliness is measured will have truly tangible effects on the experience of the individual, provide increased GSM-worker productivity and job satisfaction, and help create an environment where workers feel more valued and comfortable.

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B.7 Citations

Atherton, Timothy J, Ramon S Barthelemy, Wouter Deconinck, Michael L Ralk, Savannah Garmon, Elena Long, Monica Plisch, Elizabeth H Simmons, and Kyle Reeves. 2016. LGBT Climate in Physics: Building an Inclusive Community. College Park, MD.

Bradford, Judith, Sari L. Reisner, Julie A. Honnold, and Jessica Xavier. 2013. "Experiences of transgender-related discrimination and implications for health: results from the Virginia transgender health initiative study.(Author abstract)." The American Journal of Public Health 103 (10):1820. doi: 10.2105/AJPH.2012.300796.

Brown, John Seely, and Inc NetLibrary. 2005. Storytelling in organizations why storytelling is transforming 21st century organizations and management. Boston: Boston : Elsevier Butterworth-Heinemann.

Deal, Terrence E. 1982. Corporate cultures : the rites and rituals of corporate life. Edited by Allan A. Kennedy. Reading, Mass.: Reading, Mass. : Addison-Wesley Pub. Co.

Dulek, Ronald E. 2015. "Instituting Cultural Change at a Major Organization: A Case Study." Business and Professional Communication Quarterly 78 (2):231-243. doi: 10.1177/2329490614554991.

Dunford, Richard, and Deborah Jones. 2000. "Narrative in strategic change.(Brief Article)." Human Relations 53 (9):1207. doi: 10.1177/0018726700539005.

Faulkner, Wendy. 2009a. "Doing gender in engineering workplace cultures. I. Observations from the field." Engineering Studies 1 (1):3-18. doi: 10.1080/19378620902721322.

Faulkner, Wendy. 2009b. "Doing gender in engineering workplace cultures. II. Gender in/authenticity and the in/visibility paradox." Engineering Studies 1 (3):169-190. doi: 10.1080/19378620903225059.

Feder, Toni. 2015. "APS looks to improve climate for LGBT physicists." Physics Today 68 (3):25-27.

Flamholtz, Eric. 2011. Corporate culture the ultimate strategic asset. Edited by Yvonne Randle. Stanford, Calif.: Stanford, Calif. : Stanford Business Books.

Flamholtz, Eric, and Yvonne Randle. 2012. "Corporate culture, business models, competitive advantage, strategic assets and the bottom line." Journal of HRCA : Human Resource Costing & Accounting 16 (2):76-94. doi: 10.1108/14013381211284227.

Fossum, John A. 1974. "Urban-Rural Differences in Job Satisfaction." Industrial & Labor Relations Review 27 (3):405-409. doi: 10.1177/001979397402700305.

Frahm, Jennifer, and Kerry Brown. 2007. "First steps: linking change communication to change receptivity." Journal of Organizational Change Management 20 (3):370-387. doi: 10.1108/09534810710740191.

Garofalo, Robert, R. Cameron Wolf, Lawrence S. Wissow, Elizabeth R. Woods, and Elizabeth Goodman. 1999. "Sexual Orientation and Risk of Suicide Attempts Among a Representative Sample of Youth." Archives of Pediatrics & Adolescent Medicine 153 (5):487-493. doi: 10.1001/archpedi.153.5.487.

Gates, Gary J. 2013. "LGBT Percentage Highest in D.C., Lowest in North Dakota." Gallup Poll Briefing:2-3.

Godwin, Kate. 2013. Stonewall Top 100 Employers 2013: Michael Rubenstein Publishing.

Gottschall, Jonathan. 2013. The storytelling animal : how stories make us human. 1st Mariner books ed.. ed: Boston : Mariner Books.

Griffith, Kristin H. 2002. "The Disclosure Dilemma for Gay Men and Lesbians: "Coming Out" at Work." Journal of Applied Psychology 87 (6):1191-1200. doi: 10.1037//0021-9010.87.6.1191.

Human Rights Campaign. 2015. Stonewall top 100 employers. Human Rights Campaign Foundation.

Human Rights Campaign. 2018. Corporate Equality Index. Human Rights Campaign Foundation.

Johnston, Derek, and Mary A. Malina. 2008. "Managing Sexual Orientation Diversity: The Impact on Firm Value." Group & Organization Management 33 (5):602-625. doi: 10.1177/1059601108321833.

Kaveny, Cathleen. 2015. "Playing the Princess." Commonweal 142 (8):8.

Kjellberg, Hans, and Per Andersson. 2003. "WHERE IS THE ACTION? THE RECONSTRUCTION OF ACTION IN BUSINESS NARRATIVES." Advances in Business Marketing and Purchasing 12:13-58. doi: 10.1016/S1069-0964(03)12001-7.

Kotter, John P. 1995. "Leading Change: Why Transformation Efforts Fail." Harvard Business Review 73 (2):59-68.

Lay, William D. 2016. "Free Exercise and the Resurgence of the Religious Freedom Restoration Act." SAGE Open 6 (1). doi: 10.1177/2158244015625446.

Lewis, Laurie K. 1999. "Disseminating Information and Soliciting Input during Planned Organizational Change: Implementers' Targets, Sources, and Channels for Communicating." Management Communication Quarterly 13 (1):43-75. doi: 10.1177/0893318999131002.

Martinson, O. B., and E. A. Wilkening. 1984. "Rural-Urban Differences in Job Satisfaction: Further Evidence." Academy of Management Journal 27:199-206.

Meyer, Doug. 2015. Violence against queer people : race, class, gender, and the persistence of anti-LGBT discrimination: New Brunswick, New Jersey : Rutgers University Press.

Nauen, Rachel. 2017. Two in Five LGBT Workers Feel Bullied at Work. CareerBuilder.

Peters, Thomas J. 1984. In search of excellence : lessons from America's best-run companies. Edited by Robert H. Waterman. Warner books ed.. ed. New York, NY: New York, NY : Warner Books.

Pfeffer, Jeffrey. 2010. "Power Play." Harvard Business Review 88 (7, 8):n/a.

Pizer, Jennifer, Christy Mallory, Brad Sears, and Nan Hunter. 2012. "Evidence of Persistent and Pervasive Workplace Discrimination Against LGBT People: The Need for Federal Legislation Prohibiting Discrimination and Providing for Equal Employment Benefits."

Trasvina, John. "LGBT Housing Discrimination in 2011: A Time for Pride and Action. Washington, D.C." Huffington Post (2011).

Turner, Arthur N. 1965. Industrial jobs and the worker; an investigation of response to task attributes. Edited by Paul R. Lawrence. Boston: Boston, Harvard University, Division of Research, Graduate School of Business Administration.

Van Leeuwen, James M., Susan Boyle, Stacy Salomonsen-Sautel, D. Nico Baker, J. T. Garcia, Allison Hoffman, and Christian J. Hopfer. 2005. "Lesbian, Gay, and Bisexual Homeless Youth: An Eight-City Public Health Perspective." Child Welfare 85 (2):151-170.

Victoria Scanlan, Stefanakos. 2001. "Hatred in the hallways." The Advocate (840):18.

Walker, H. Jack. 2007. "Factors influencing organizational change efforts: An integrative investigation of change content, context, process and individual differences." Journal of Organizational Change Management 20 (6):761-774. doi: 10.1108/09534810710831000.

Wang, Peng, and Joshua L. Schwarz. 2010. "Stock price reactions to GLBT nondiscrimination policies." Human Resource Management 49 (2):195-216. doi: 10.1002/hrm.20341.

Westover, Jonathan H. 2010. "Managing organizational change: change agent strategies and techniques to successfully managing the dynamics of stability and change in organizations." International Journal of Management and Innovation 2 (1):45.

Yoder, Jeremy B. 2016. "Queer in STEM: Workplace Experiences Reported in a National Survey of LGBTQA Individuals in Science, Technology, Engineering, and Mathematics Careers." Journal of Homosexuality 63 (1):1-28.

APPENDIX C. CRITICAL INCIDENT ASSESSMENT AS A TOOL TO REFLECT ON STUDENTS' EMOTIONAL RESPONSE DURING INTERNATIONAL EXPERIENCES CRITICAL INCIDENT ASSESSMENT AS A TOOL TO REFLECT ON STUDENTS' EMOTIONAL RESPONSE DURING INTERNATIONAL EXPERIENCES

This work is currently under review in the American Society of Engineering Education conference in Montréal in 2020. For this paper, I am first author and provided the largest amount of intellectual merit as such. The work was written collaboratively, though I was largely in charge of the data analysis for this work with mentorship and collaboration from my co-authors.

C.1 Introduction

In a global society, cultural competence - or the ability to work with, learn from, and interact with people from belief systems and cultures other than one's own [1] - is a necessity. This is as true for engineering as it is for many other disciplines. The 'critical incident technique' (CIT), also called the critical incident approach or assessment (CIA), has been used as a developmental tool to build cultural competence and knowledge when students are immersed in a foreign culture. [2] This work will discuss the experiences and use of the CIA by an interdisciplinary, multicultural group of graduate students brought together by the National Science Foundation (NSF)-funded Integrative Graduate Education and Research Traineeship (IGERT) program "Global Traineeship in Sustainable Electronics." During its tenure, three cohorts comprised of students from Purdue University and Tuskegee University participated in the program. An integral part of this two-year traineeship was an international trip to India. This visit was designed to promote several of the program's objectives: 1) developing systems thinking and interdisciplinary collaboration relative to sustainability and global supply chains, 2) encouraging leadership in cross-cultural teams, and 3) help students recognize barriers while building bridges. The CIA was initially introduced as a tool to help students reflect on their experiences abroad while providing a safe and supportive environment for learning under the guidance of experts in sustainability and electronics manufacturing.

While the international trip was expected to be immensely valuable for students, it was anticipated that the students, who were from a variety of educational, personal, and cultural backgrounds, would likely not have experienced traveling abroad, especially for academic purposes. Additionally, while the students could witness the entire lifecycle of an electronic device in India, it is also a country with remarkably different cultures than the USA surrounding sustainability and worker safety. Introducing graduate students to international cultures can introduce significant emotional impact, or culture shock, which could result in biased analysis of situations and thus a biased determination of whether a practice was sustainable or not. [3, 4] Therefore, the CIA was reframed in the context of sustainability to help students focus on the reason for their visit as well as build cultural competence in professional and societal practices internationally.

This study aims to understand whether the CIA framework was able to enhance personal and group intercultural development in the context of sustainability through use of reflection and discussion. With the motivation to strengthen this development most effectively, this study investigates the strengths and limitations of the CIA tool used to identify bias, understand intercultural sustainability, and generate cultural awareness. This study also provides insight into group and environmental attributes that may be conducive to successful application of this tool. Surveying of CIA users was completed using a mixture of matrix questions, Likert scale questions, ranking questions, and open-ended questions that covered topics such as environmental factors (e.g. time of day and location), group dynamics (e.g. group size and demographics) and level of familiarity with the tool. It is the hope of the authors that this work will help future students and faculty better understand the deeply complex, intersectional topics within sustainability when viewed through an international, cultural context.

C.2 Relevant Literature Review and Background

Flanagan introduced the "critical incident technique" (CIT) in 1954 as a systematic way to record observations about a critical incident in an objective manner for use in practical problem solving. [5] Fitzgerald defines a critical incident as "…distinct occurrences or events which involve two or more people; they are neither inherently negative nor positive, they are merely distinct occurrences or events which require some attention, action or explanation; they are situations for which there is a need to attach meaning". [6] Over the subsequent decades, the CIT (or CIA) has been adapted for many purposes, including cultural competence training and group critical incident stress debriefing.

McAllister et al (2006) described the need for development of an intercultural skill set as a requisite for professional competence. [2] Universities play an important role in developing cultural knowledge and competencies in their students [2] which is reflected in the ABET engineering accreditation requirements for student outcomes (Criterion 3, Outcome 4). [7] Experiential education (e.g. a study abroad program) can be an effective method for developing these skills , but 'requires reflection and critical analysis' in order to transform experience into knowledge. [8] This concept is supported by Sieck et al, who found that critical reflection, such as the activities encouraged by CIT, is aligned with the metacognitive strategies that were commonly displayed by cross-cultural experts. [9] Further, Lutterman-Aguilar and Gingerich contend that critical analysis and reflection are a collective process and dialogue with others is key to helping a student to 'move beyond their own perspectives to new understandings.' [8]

Cultural bias is "the tendency to interpret and judge phenomena in terms of the distinctive values, beliefs, and other characteristics of the society or community to which one belongs". [1] Understanding one's own biases and prejudices can help one develop skills to enhance interactions and engagement with individuals from another culture. Biases begin from our personal backgrounds, e.g. experience and information that we gather early in life, and are made more complex because they intersect with our culture and identity. Critical reflection allows us to identify and acknowledge both explicit and implicit (unknown or hidden) bias, [10] and is an important step in becoming more culturally competent. [2, 11]

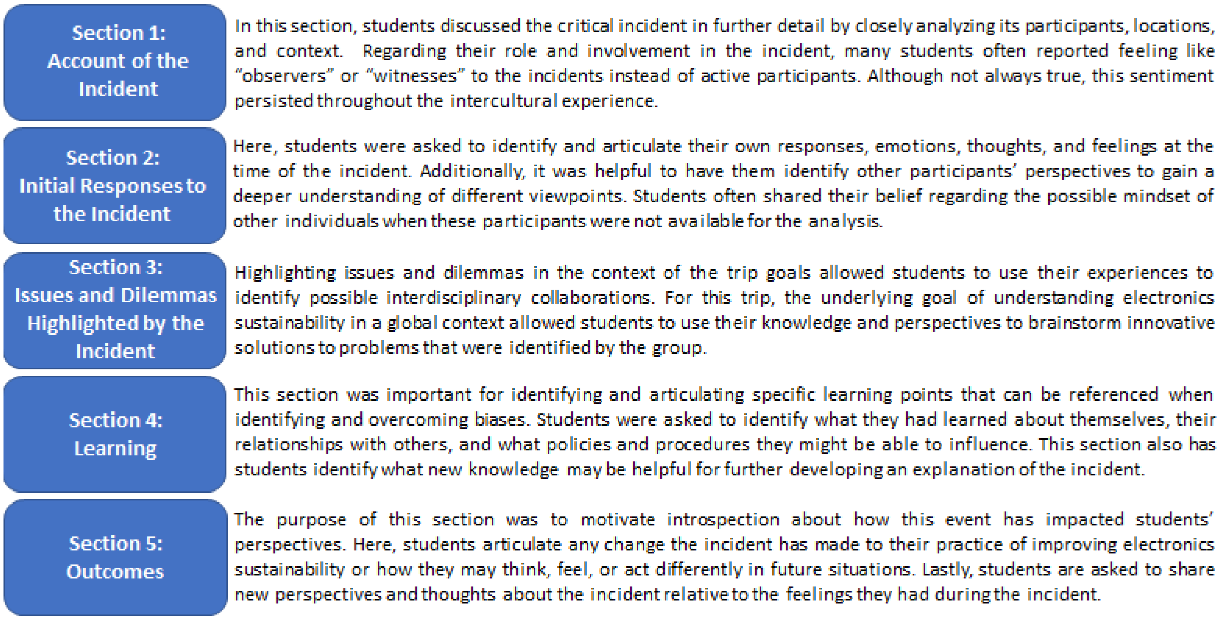
Cultural competence may be especially important for training students in global electronics sustainability due to the global nature of the electronics supply chain and associated waste (e-waste). Illegal, transboundary shipments of e-waste, unfair labor practices, mineral extraction practices which fuel conflict, and other environmental and social issues associated with the electronics industry are complex and require international and cross-cultural solutions. Broadly, the UN Organization for Economic Co-operation and Development conducted a global assessment to measure young people's cultural competence, as they consider globally competent knowledge, skills, attitudes and values as vital for promoting 'sustainable development and collective well-being.' [12]

In addition to developing cultural competence, the critical reflection required by the CIA can act as a debriefing tool for critical incidents that may cause stress or anxiety for participants. [13] Critical Incident Stress Debriefing (CISD) is a common practice for emergency personnel (e.g. police, firefighters, nurses) to deal with stress after a traumatic event; [13] however, it has also been adapted for other settings, including study abroad programs, where it acts as an "emotional first-aid." [14] One of the main purposes of a CISD is to mitigate the impact of a critical incident through timely discussion and reflection upon the incident. While the primary intent of the CIA in the context of the IGERT program was to build cultural competence through reflective critical thinking, the tool supported the building of trust, respect and understanding among the group, which is often the result of peer supported CISD. [15]

C.3 Background Information on Sustainability CIA

CIA-Sustainability Framework

Within the IGERT program, this technique was adopted in order to help the students understand the complex, intersectional challenges associated with the electronics life cycle during their trip abroad to India. The structure of the CIA that was utilized for this can be found in the Supplemental Information to this document. They include: Section 1) Account of the Incident, 2) Initial Responses to the Incident, 3) Issues and Dilemmas Highlighted by the Incident, 4) Learning, 5) Outcomes. The goals of the sections are explained in further detail (Figure C.1). As discussed earlier, the purpose of the structure of the CIA was to enable students to understand the complex cultures and challenges in which they were immersed to better understand the sustainable (or unsustainable) practices they were witnessing. Walking students through the account, their response, learning opportunities, and outcomes was designed to purposefully enable this process to take place, while additionally fostering structured discussion within the group.



Section 1: Account of the Incident	In this section, students discussed the critical incident in further detail by closely analyzing its participants, locations, and context. Regarding their role and involvement in the incident, many students often reported feeling like "observers" or "witnesses" to the incidents instead of active participants. Although not always true, this sentiment persisted throughout the intercultural experience.
Section 2: Initial Responses to the Incident	Here, students were asked to identify and articulate their own responses, emotions, thoughts, and feelings at the time of the incident. Additionally, it was helpful to have them identify other participants' perspectives to gain a deeper understanding of different viewpoints. Students often shared their belief regarding the possible mindset of other individuals when these participants were not available for the analysis.
Section 3: Issues and Dilemmas Highlighted by the Incident	Highlighting issues and dilemmas in the context of the trip goals allowed students to use their experiences to identify possible interdisciplinary collaborations. For this trip, the underlying goal of understanding electronics sustainability in a global context allowed students to use their knowledge and perspectives to brainstorm innovative solutions to problems that were identified by the group.
Section 4: Learning	This section was important for identifying and articulating specific learning points that can be referenced when identifying and overcoming biases. Students were asked to identify what they had learned about themselves, their relationships with others, and what policies and procedures they might be able to influence. This section also has students identify what new knowledge may be helpful for further developing an explanation of the incident.
Section 5: Outcomes	The purpose of this section was to motivate introspection about how this event has impacted students' perspectives. Here, students articulate any change the incident has made to their practice of improving electronics sustainability or how they may think, feel, or act differently in future situations. Lastly, students are asked to share new perspectives and thoughts about the incident relative to the feelings they had during the incident.

Figure C.1: Framework for the CIA used by the IGERT- "Global Traineeship in Sustainable Electronics" program.

Logistics

During the international trip students performed a CIA daily. CIAs were performed in a group, with group sizes between 7 and 20 people depending on the cohort. CIAs were performed in a variety of places including the hotel lobbies or patios, as well as the tour buses. Group discussions took place in one of two arranges: sitting in a circle when space was available or in rows (when conducted on the tour bus). On at least one occasion, two groups were formed to conduct the CIA as the group had to travel on two separate buses. Depending on the group's travel schedule, CIAs were conducted from early morning (a rare occurrence) to late evening. Depending on the location, the background noise level could be quite loud or very quiet.

Running the CIA

Some groups adopted an organizational structure for the CIA, in which a volunteer leader would mediate the discussion and a volunteer note taker would record responses. Some cohorts also elected to have time-limits on the discussion time. In that case, an optional role of a timer- a person to keep track of the time and set the pace- was also elected. The roles rotated everyday to share the responsibility. Group discussions were student led and professors, although present, rarely participated unless to address a technical question or provide cultural context if they felt comfortable.

C.4 Methods

A Qualtrics survey was developed to collect students' opinions and feedback about the use of the CIA-sustainability framework. Survey questions consisted of matrix questions, Likert scale questions, ranking questions, and open-ended response questions which can be found in the supplemental information. Student responses were normalized by the total number of responses per question to obtain percentages of each response. For scaled agree/disagree-style questions (e.g. Question 1) students who answered somewhat or strongly agree were summed to be the “agree” category for analysis, whereas all other answers were organized into the “did not agree” category. Additionally, the median and mode for each answer are reported, as they have been found to better show trends in the data for Likert-style questions than the mean. [16] Chi squared analysis was used to determine statistical differences in Likert questions, with “agree” and “not agree” used as the variables of interest. Extended responses were used to clarify trends and provide context.

Students from all three IGERT cohorts were polled. Of the 28 students who were associated with the program, between 13-15 responded (46-53% response rate) as 2 users began but did not complete the survey

C.5 Results & Discussion:

Understanding International Sustainability

The CIA was introduced to help students process/assess their experiences during the industrial visits, like those in the United States and in India, where students interfaced with various stakeholders in electronics manufacturing. The majority of students felt that their previous IGERT education affected their perception of both environmental and social sustainability internationally (93.3%) and that the CIA helped them understand the sustainability or sustainable practices of the places and organizations they visited (100%) while creating a space for them to share their thoughts and feelings (100%), listen to their peers (100%), and ask additional questions (100%).

During visits, students typically met with various representatives of the company and toured the location in which they might learn about processes, how the company functions, and the corporate responsibility initiatives of the company, including efforts to make the systems within the company and within communities more sustainable. Having been taught primarily North American standards and practices of sustainability in the classroom, students may enter industrial settings with preconceived notions of what sustainability should be or looks like in industry practices, government involvement, etc. When asked whether they found any practices in India to be more or less sustainable when viewed through the lens of a North American measure of sustainability, all students agreed that they did (100%). Having previous knowledge of companies in the USA provided a point of reference for many students as did their personal experience which came up in their comments. Several students commented that while many facilities were up to USA standards taught in the classroom, others were not and, in those cases, cited specific violations such as the "disregard for employee health and safety at the lead acid battery factory," and "smell of chemicals…that signified the lack of health regulations and PPE required in comparison to the USA." At one of the companies, students were presented with the idea that waste materials (a phenolic resin used in manufacturing electronic components) could be used to produce bricks. These bricks were given away to whoever picked them up off the street. By the company, it was presented as more sustainable because it allows the waste to be repurposed and the building materials are free (therefore would go to low income people that build their houses incrementally over time). Two students expressed concern about this practice, because while it appears more sustainable on the surface, there could be safety concerns with using these materials which may or may not be covered by environmental and OSHA-type regulations for human and environmental exposure.[1] However, while the students noted differences in worker safety cultures, students also identified more socially sustainable practices in India such as the practice of "promoting from within the company- rather than external hiring- which makes retention higher and employees more motivated," which was a common culture among many companies toured in India.

Students overwhelmingly agreed that the CIA helped them reflect deeply on at least one critical incident (78%), identify incidents where the group had conflicting perceptions (100%), and on at least one occasion, changed their understanding of an incident (92.2%). All of these factors could be responsible for the ability for students to understand the complex dynamics of the incidents described in the responses to the survey. Students additionally identified that the CIA enabled them to ask questions and get clarification about critical incidents (100%), made them aware of critical incidents they may not have noticed (100%), and encouraged further discussion after the CIA was over (92.2%).

Identification of Personal Bias & Enhancing Cultural Competence

Assessing sustainability practices abroad necessitates a level of cultural competence in which acknowledgement and understanding of one's own personal biases is key. Students were polled to ask whether they felt the CIA was a tool that enabled them to identify their personal biases (Figure C.2). Students largely felt that the CIA enabled them to identify their personal biases (80%), and believed that these biases provided unique perspectives during the discussion (73.3%). Students additionally identified that their personal biases affected their perception of at least one critical incident (73.3%), and cited on more than one occasion an experience during their time visiting a site where women were employed to sort and categorize solid waste for composting. One student remarked that they were shocked to see women employed to 'sort trash'. This was especially remarkable to the student because the women worked in conditions that were visibly unclean and with little protective clothing, while their male supervisors seemed to be "sitting around". The student was initially quite upset by the scene, but by critically reflecting on the incident through CIA, realized that they were imposing their own ideas of family and workplace culture. After discussing the incident with the group, the student realized that these working conditions were vastly preferred to what the women were previously doing and this job, in contrast, was providing steady work and education for their children. The student concluded that the incident was far more complex than they initially thought and had to be considered within the context of both Indian culture and cross-cultural concepts of sustainability. This example indicates quite clearly the transition in thinking for the student made possible by the CIA and that through fostering discussion it could increase their cultural competence through identifying their personal biases.

Respondents were unclear as to whether their responses to critical incidents affected their ability to analyze the situation from an unbiased perspective (53.4% Agree, Mode: Neutral). These results indicate that students had an initial perception of what was happening in the moment they were seeing it, but upon reflection were not necessarily biased in their analysis of what happened - as evidenced by the incidents involving the phenolic bricks, safety concerns, and social responsibility. This result is perhaps a product of the group being observers for most critical incidents, but is likely a product of the use of the CIA as indicated by survey responses.

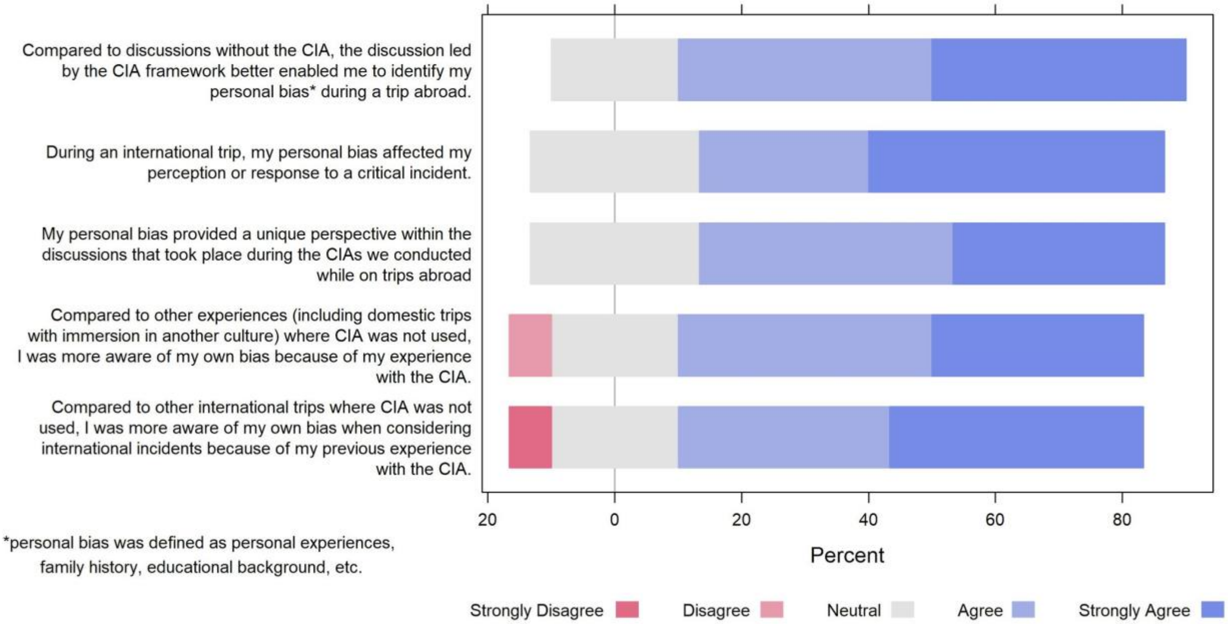


Figure C.2. Student responses pertaining to personal bias.

The CIA was not only a tool useful for identifying personal bias during the trip the CIA was practiced, but it also made students more aware of their biases on future experiences. Students identified that the use of the CIA during one international trip made them more aware of their own biases on other international trips (73.3%) and domestic trips (73.3%) where they did not use the CIA. Respondents additionally indicated long-term impacts of the CIA when they indicated that, “frameworks such as this one (have) assisted me during my transition/tenure to/in industry,” and by indicating they discussed these ideas with their friends outside of the program. These results indicated that students felt a much more long-term effects from the use of the CIA in this program, but perhaps needed a few interactions with it during a trip to see that it was useful.

Group Dynamics

Students were asked to help determine whether the CIA affected group dynamics and thereby enhanced discussion on critical incidents (Figure C.3). Students felt that the CIA allowed them to listen to their peers' feelings/thoughts about a critical incident (100%), express their own feelings about a critical incident (92.3%), and develop trust in the other students during the trip (68.5%). Students may have been more willing to share their feelings with each other might be because they trusted each other. However, poor group dynamics can potentially serve as a barrier to communication, which was observed in at least one IGERT cohort. From follow-up discussions, it was determined that students with strong opinions and personalities can potentially result in an unproductive CIA environment. This idea was supported by further explanations from respondents who indicated, "The framework was useful to foster discussion, but its usefulness was partially limited by the willingness of others to engage."

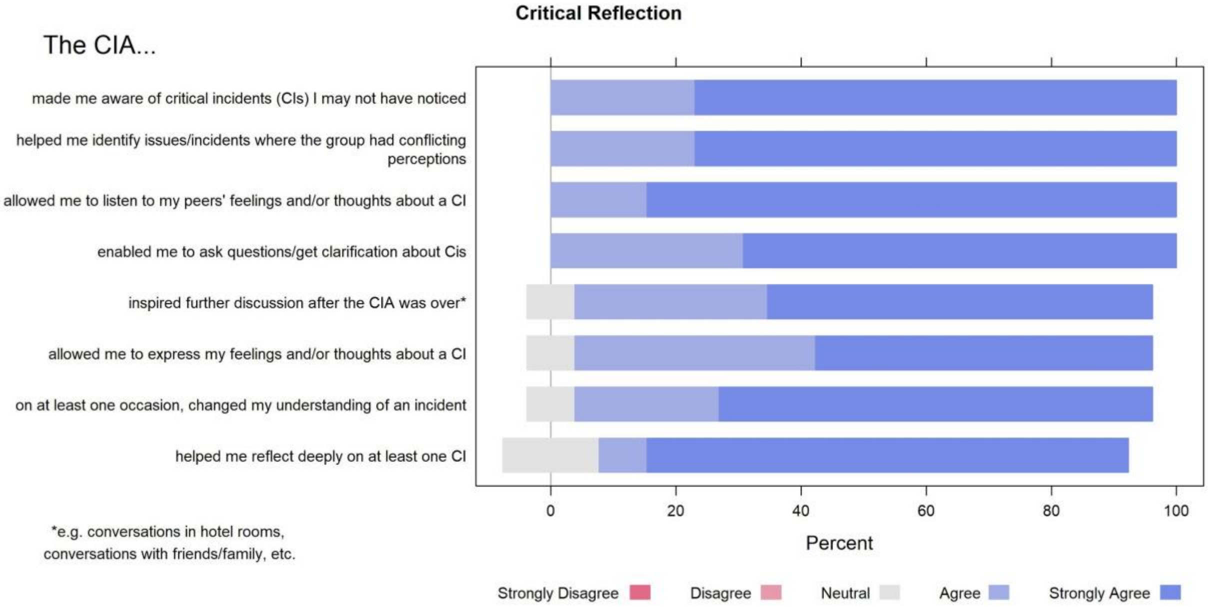


Figure C.3: Student responses pertaining to the use of the CIA to facilitate discussion and its impact on group interactions.

Changes in dynamics between cohorts affected the effectiveness of the CIA, as reported by follow-up interviews. Interview respondents indicated that groups who were more interested in learning from others from the visited area tended to more positively utilize the CIA. Additionally, while the respondents from this study indicate that they felt that the CIA helped them develop trust, there were other opportunities within the program to develop trust. This included once-per-semester in-person meetings and informal gatherings including dinner at restaurants, homes of faculty and homes of students in the program. Students indicated that the CIA was an important aspect to this trust development.

When performing CIAs, students felt their CIA was chosen about half of the time or slightly less. However, students did not feel that the critical incident they suggested was less important when the group chose to analyze a different critical incident (69.2%). This could have been because students often only identified a few (1-3) critical incidents per day and perhaps felt they were equally important but only one needed further discussion/clarification from the group. While students reported that they were comfortable sharing their ideas and thoughts with the group (84.6%), they did not necessarily feel they contributed equally to their peers (53.1% Agreed, Mode: Neutral). This could be because students did not feel equipped to discuss the complex cultural aspects of the events which took place, and instead relied on their peers and faculty to provide this perspective. Students felt significantly more interested in participating in the CIA when the group had different thoughts about an incident (92.3%) than when the group had the same thoughts about an incident (46.1%) (p=0.01) (Figure C.4). When the group largely agreed, students may have felt other people were saying what they thought and didn't need to participate to make sure their voice was heard. Another explanation could be that students felt the CIA became more of an exercise when students agreed rather than an opportunity for personal growth. Regardless, it might suggest the importance of having a diverse group of people who have differing opinions, personal experiences, etc. to provide to the conversation.

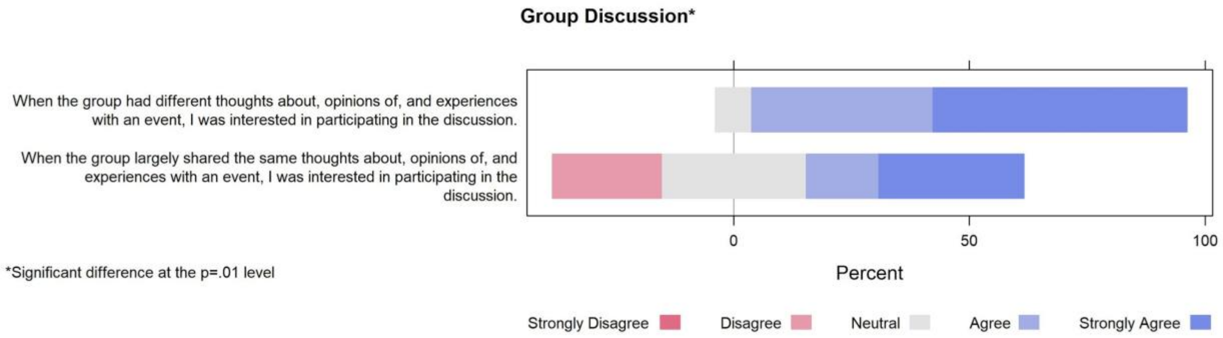


Figure C.4. Student responses on their willingness to participate when students shared opinions versus when they did not.

When polled, respondents indicated that they felt the CIA was a useful tool for enhancing group discussions (100% Agreed). Respondents felt, in retrospect, that the CIA was more useful as a tool for supporting group discussions than they originally anticipated when it was first introduced (69.4% Agreed) (p=0.02). It is suggested that the CIA's ability to help students listen and express their feelings and develop trust at least played a part in the ability for the tool to enhance discussion.

Environment

Students were polled about the ideal environment in which to perform the CIA. Students were asked about the ideal group size, time to completion, lighting in the room, how the chairs were arranged, and other factors. The respondents for this survey indicated ideal CIA environment is a group of 5-10 people (69.2%), is 31-60 minutes long (84.6%) and takes place in the afternoon (Score: 42). Morning (50%) and late night CIAs (50%) were the only options listed as a last choices indicating that these were not preferred times by many of the respondents. Most CIAs fell within the 30-90 minute timeframe on average, as suggested by follow up interviews with respondents. This indicates that if students would prefer to have a CIA in less than 60 minutes they should use some method to limit the time of discussion. Additionally, as respondents indicated that the CIA inspired further conversation after the CIA was complete, it is important to remember that the CIA may not be fully resolved in the time limit. Encouraging students to continue conversations after the CIA could potentially be beneficial for their personal development.

Respondents indicated that the space affected their willingness to participate in the CIA (69.2%) and that the students should be situated in a circle (91.7%). Students, surprisingly, indicated that the room does not need to be well-lit (76.9%). This could be explained by the use of tablets with back-lit screens when filling out the CIA which could be used in the dark. However, as many CIAs were performed on buses and moving vehicles, it is suggested that students find a way to situate themselves in a circle in whatever space they occupy. Follow-up interviews suggested that students who did not wish to participate in a CIA could more easily avoid engaging when not in a circle, but could not avoid participating as easily when situated in a circle.

While a majority of respondents indicated they get motion sickness when writing in a moving vehicle, only 40% of them indicated that it affected their participation in the CIA. This result could possibly be explained by the fact that only one student needed to serve as the scribe, and students could participate in the CIA without serving in that role. Additionally, students on the trips were aware of who was motion sick and would often volunteer to scribe in their place. That being said, the roads on many international trips were bumpy resulting in some students getting motion sickness regardless, which could explain the 40% of cases where students got motion sick.

Most students (69%) felt uncomfortable conducting the CIA where people could overhear and that the level of background noise affected their participation (53.9%). On at least one occasion the bus driver overhearing a conversation during the trip made respondents uncomfortable, as the students noticed the driver silently reacting to what was said. However, students were more comfortable when faculty, who did not always participate, were present in the group (61.6%). These results suggest the discomfort students observed was particularly with regard to people listening that did not know the context of the conversation. Performing the CIA in a private space where others could not overhear the conversation, or providing context to the conversation to the people who could overhear the conversation (e.g. bus drivers or tour guides) when that is unavoidable, may help prevent this. It is encouraged to include tour guides and bus drivers to participate in the CIA when they would like to, even though this practice was not implemented during this trip.

C.6 Best Practices Summary

Over the course of seven years, the CIA was used by the Global Electronics Sustainability IGERT program. Our best practices for creating an environment for participating in the CIA, based on student survey feedback, is shown in Table 1.

Table 1. Best practices based on student feedback.

Size of Group	5-10 people
Time to Complete CIA	30-60 minutes
Time of Day	Afternoon
Type of Space	Private & Quiet
Arrangement of Students	Circular (Facing Each Other)

C.7 Conclusions

The CIA framework was adapted for the purpose of helping graduate students better understand sustainability internationally and increase their cultural competence- skills essential to their future success and inline with the goals of the IGERT- "Global Traineeship in Sustainable Electronics" program. Responses suggest that the CIA was a useful tool for identifying personal biases, increasing cultural competence, enhancing group discussions, and understanding sustainability in an international context. Group dynamics were critical to the success of the CIA, with a willingness to participate being of paramount importance. Best practices for the environment, time, and group structure were ascertained from respondents to this study. It is the hope of the authors of this work that future educators who wish to adopt this tool into their programs can do so with best practices in mind to ensure the CIA is maximally impactful.

C.8 Acknowledgements

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C.9 Bibliography

[1] American Psychological Association. "APA Dictionary of Psychology: Cultural Bias." (accessed 2020).

[2] L. McAllister, G. Whiteford, B. Hill, N. Thomas, and M. Fitzgerald, "Reflection in intercultural learning: examining the international experience through a critical incident approach," Reflective Practice, vol. 7, no. 3, pp. 367-381, 2006, doi: 10.1080/14623940600837624.

[3] H. C. Triandis, Theoretical concepts that are applicable to the analysis of ethnocentrism. Applied cross-cultural psychology.

[4] R. F. Chapdelaine and L. R. Alexitch, "Social Skills Difficulty: Model of Culture Shock for International Graduate Students," Journal of College Student Development, vol. 45, no. 2, p. 167, 2004, doi: 10.1353/csd.2004.0021.

[5] J. C. Flanagan, "The critical incident technique," Psychological Bulletin, vol. 51, no. 4, pp. 327-358, 1954, doi: 10.1037/h0061470.

[6] M. Fitzgerald, J. Kingsley, Ed. Establishing cultural competency for health professionals (Anthropological approaches to psychological medicine.). London, 2000.

[7] ABET, "Criteria for Accrediting Engineering Programs, 2019 - 2020," 2019.

[8] A. Lutterman-Aguilar and O. Gingerich, "Experiential pedagogy for study abroad: educating for global citizenship," Frontiers: The Interdisciplinary Journal of Study Abroad, vol. 8, pp. 41-82, 2015.

[9] W. R. Sieck, J. L. Smith, and L. J. Rasmussen, "Metacognitive Strategies for Making Sense of Cross-Cultural Encounters," Journal of Cross-Cultural Psychology, vol. 44, no. 6, pp. 1007-1023, 2013, doi: 10.1177/0022022113492890.

[10] C. Motzkus et al., "Pre-clinical medical student reflections on implicit bias: Implications for learning and teaching," PLoS ONE, vol. 14, no. 11, 2019, doi: 10.1371/journal.pone.0225058.

[11] A. Blanchet Garneau, "Critical Reflection in Cultural Competence Development: A Framework for Undergraduate Nursing Education," The Journal of nursing education, vol. 55, no. 3, p. 125, 2016, doi: 10.3928/01484834-20160216-02.

[12] Development Organisation for Economic Cooperation and, "Preparing Our Youth for an Inclusive and Sustainable World: The OECD PISA Global Competence Framework," ed: OECD Publishing, 2018.

[13] J. T. Mitchell, "When disaster strikes... The critical incident stress debriefing process," Journal of Emergency Medical Services: JEMS, vol. 8, no. 1, pp. 36-39, 1983.

[14] International Sustainable Development Studies Institute. "Emotional First Aid (EFA) Course." (accessed 2020).

[15] National Office of Fire and Aviation, "Critical Incident Stress Management: What to Expect," 2020.

[16] A. Joshi, S. Kale, S. Chandel, and D. K. Pal, "Likert Scale: Explored and Explained," British Journal of Applied Science & Technology, vol. 7, no. 4, pp. 397-403, 2015.

APPENDIX D. WHAT'S THE T, CIS? DISCUSSING GENDER IDENTITY AND SEXUAL ORIENTATION IN TMS

This work was published in JOM, the TMS magazine as a follow-up to a symposium that I helped organized. I am listed as the sole author of this work and wrote it entirely by myself with little mentorship or input from others.

Introduction

While currently TMS does not have any metrics on how many people in our society identify as lesbian, gay, bisexual, and/or transgender (LGBTQ+), recent estimates in the literature suggest that anywhere from 3.0±0.5% of the population of the United States identifies as LGBTQ+.[1, 2] Per the 2015 Annual Report by TMS, applying these metrics to our society we would anticipate anywhere from 300-500 members of TMS and nearly 200 attendees at our national meeting to identify this way. When expanded to the actual size of the population of the United States, similar estimates would indicate that 5-8 million employees in America identify as LGBTQ+. While it is possible for many LGBTQ+ people to hide their sexual orientation or gender identity in the workplace and at our national meetings, many people cannot. This is because they physically wear their identity at work or at a conference, such as people who are mid-transition and people who identify outside of the gender binary (e.g. genderqueer). As this information in the scientific literature is becoming more readily available, it is increasingly more important for our discipline to continue to discuss methods to make our international meetings and individual workplaces more inclusive to people of LGBTQ+ identity. Especially when the society begins to look at methods to make these spaces more inclusive to everyone.

TMS 2019 Diversity Symposium

There was significant discussion on LGBTQ+ topics during the TMS annual meeting this year, with 3 speakers giving descriptive, unique explanations of their experiences not only within TMS, but also within the discipline. While many have begun to understand the many, complex sexual orientations with which people identify, there are many who still do not understand gender identity. Throughout the symposium, many different figures were used to help explain these topics to a materials engineering audience. One speaker used chemical bonds to explain the difference between cisgender, identifying with the gender you are assigned at birth, and transgender, identifying with the gender that you experience (Figure 1).[3] A phase diagram was also used to help explain the complex gender schema, where fraction of femininity is used as the additive agent (Figure 2).[3]

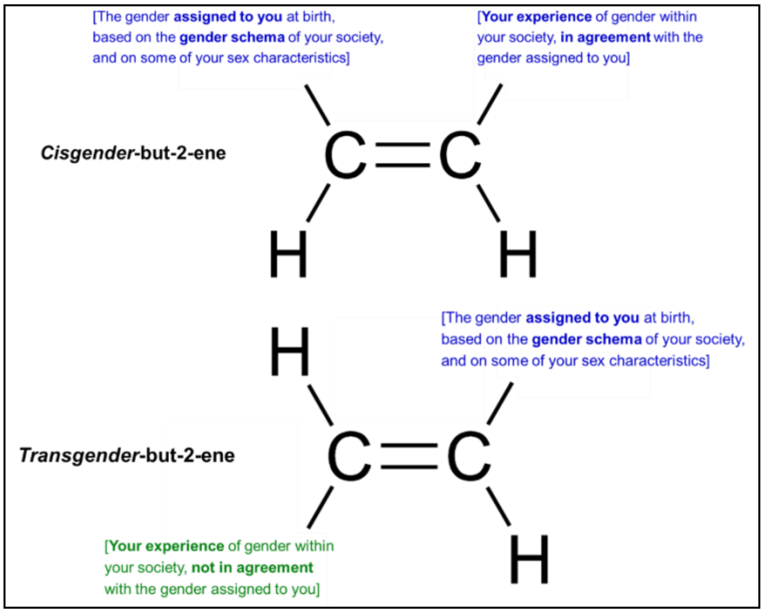

Figure 7.1: Using cis- and trans-but-2-ene to explain gender identities.3

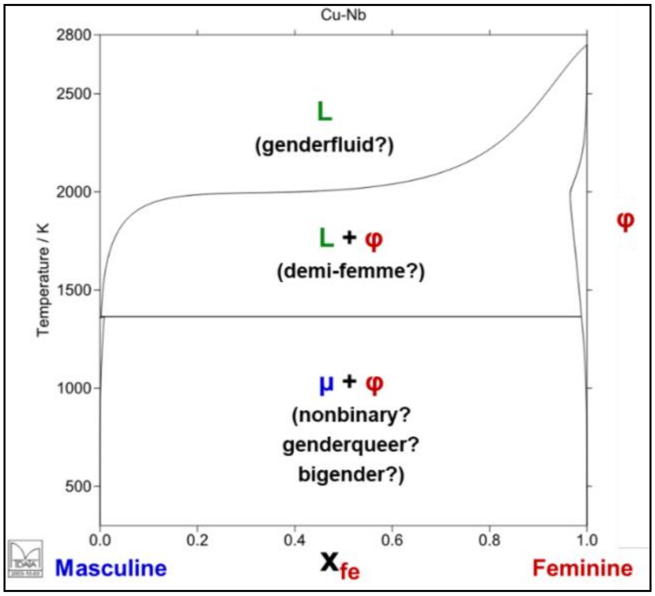

Figure 7.2: A phase diagram is used to visualize gender identity.3

One speaker at the symposium, KC Cunningham, addressed the needs of individuals who identify as transgender. These needs take many forms, but more broadly are psychological needs, social needs, legal needs, and medical needs. Psychological needs include 1) it is easy to discover your identity, 2) it is possible to meet others like you in your daily life, and 3) your identity is not criminalized where you live. Social needs include 1) coming out does not put you in physical danger or 2) you will still be welcome in your social circles after coming out. Legal needs include 1) having legal protections from harassment and losing your job for coming out and 2) protection from the repeal of such protections. Medical needs include 1) living near a trans-friendly doctors and 2) having trans-friendly health insurance. True support only happens when psychological, social, legal, and medical needs intersect positively (Figure 3).[3]

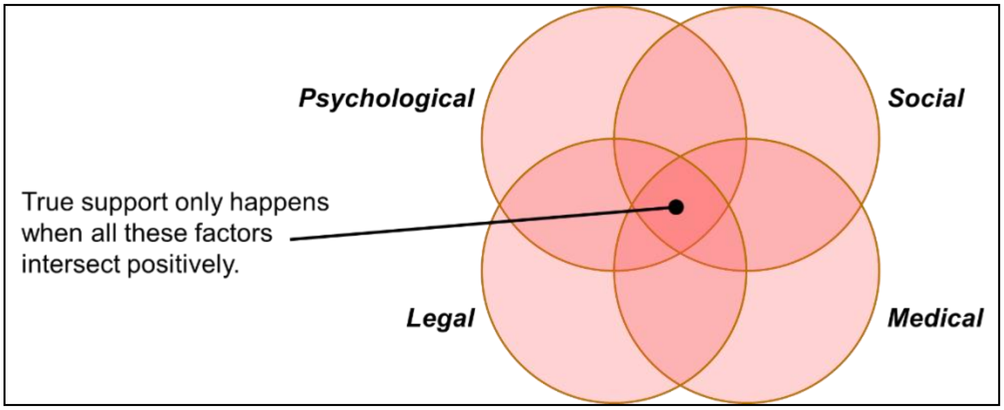

Figure 7.3: A visualization of some basic needs for transgender individuals.3

Lessons Learned

The needs of LGBTQ+ individuals are not significantly different from other populations of people. Increasing the visibility and providing opportunities for LGBTQ+ people to connect to each other within our society can help individuals feel more connected to TMS. However, making sure that transgender individuals have their basic needs met is an important aspect of inclusion within this complex community, and TMS must strive to provide these needs to ensure it is inclusive of everyone.

In the last year, a working group created within the TMS Diversity Committee has begun increasing the availability of LGBTQ+ related programming and visibility throughout the society as a whole, but also at the TMS annual meeting (and affiliated meetings). The TMS PRIDE working group has hosted networking nights, helped organize the diversity breakfast, led symposia, and have hosted informal networking events throughout the annual meetings. Please contact tmspride@tms.org for further information about getting involved in this working group on this topic.

Citations

1. Johnston, D.; Malina, M. A., Managing Sexual Orientation Diversity: The Impact on Firm Value. *Group & Organization Management* **2008,** *33* (5), 602-625.
2. Gates, G. J., LGBT Percentage Highest in D.C., Lowest in North Dakota. *Gallup Poll Briefing* **2013**, 2-3.
3. Cunningham, K. (2019, March). *T Time: How to Welcome and Support People of All Genders* Presented at The Minerals Metals and Materials Society National Meeting 2019, San Antonio, TX.

APPENDIX E. CURRENT CHARACTERIZATION METHODS FOR CELLULOSE NANOMATERIALS: ELEMENTAL ANALYSIS

This work was published in *Chemical Society Reviews* as a larger work published with many collaborators and is Chapter 4 of that work. I wrote this portion of the document in collaboration with Jeffrey Youngblood. The text was written entirely by me with Dr. Youngblood's advice along the way. The citations and work were provided by me as the process went along.

Foster, E. J.; Moon, R. J.; Agarwal, U. P.; Bortner, M. J.; Bras, J.; Camarero-Espinosa, S.; Chan, K. J.; Clift, M. J. D.; Cranston, E. D.; Eichhorn, S. J.; Fox, D. M.; Hamad, W. Y.; Heux, L.; Jean, B.; Korey, M.; Nieh, W.; Ong, K. J.; Reid, M. S.; Renneckar, S.; Roberts, R.; Shatkin, J. A.; Simonsen, J.; Stinson-Bagby, K.; Wanasekara, N.; Youngblood, J., Current characterization methods for cellulose nanomaterials. *Chemical Society Reviews* **2018,** (47), 2609-2679. DOI: 10.1039/C6CS00895J - Reproduced with permission from The Royal Society of Chemistry.

Introduction

Elemental analysis (EA) is composed of a variety of techniques that measure the elemental composition of a sample, as listed in Table 2. It is useful when trying to verify different elements within a sample to help ascertain the structure of, or for measuring the purity of, a known or unknown compound. EA techniques are often the fastest and most inexpensive methods to determine the purity of samples. These methods of chemical analysis are particularly useful in CNMs because they can provide validation and quantification of chemical modification, can help identify sulfur and other elements in a sample, can provide verification of acid hydrolysis of cellulose-containing compounds, and can assist in determining impurities in materials containing CNMs.While EA methods often cannot be used alone to determine the structure of a compound, they can be used to obtain useful complementary information for further verification. It is important to choose the most applicable method of EA when characterizing CNMs. This review will focus on carbon hydrogen nitrogen sulfur elemental analysis (CHNS EA), secondary ion mass spectrometry (SIMS), X-ray photoelectron spectroscopy (XPS), auger electron spectroscopy (AES), energy dispersive X-ray spectroscopy (EDS or EDX), and atomic emission spectroscopy techniques including inductively coupled plasma (ICP). This is not to say these are the only techniques possible for such characterization, but these methods were determined the most valuable for characterizing CNMs. A decision tree is given in Fig. 7 to guide the reader how to choose which technique to use. A helpful summary of all of the EA methods is provided in Table 2.

CHN, CHNS, CHNS-O, and CHNS-X EA

CHN EA is used to characterize the major elements of an organic substance. The theory is based upon the Dumas method where in pure oxygen at high temperature (above 1000$_o$C) all available carbon in a sample will react to form carbon dioxide, all available hydrogen will react to become water, all nitrogen will react to become nitrous oxides[1]. Advancements in this technology have allowed for additional chemicals to be characterized including sulfur using barium sulfate (CHNS),[2] oxygen using carbon and copper oxide (CHNS-O),[3] and even halogens using silver nitrates (CHNSX)[4] but in order to detect these elements an add-on to the device or a completely new detector is required.

After initial combustion, chemicals other than carbon (C), hydrogen (H), nitrogen (N), sulfur (S), and oxygen (O) in the sample, are converted to combustion products (such as chlorine into hydrogen chloride) which are absorbed by a variety of absorbents so they do not contaminate the output. The desirable combustion products are swept out of the combustion chamber by an inert gas, helium. The gas flows over high purity copper, which is used to remove any un-reacted oxygen not consumed in the initial combustion and to convert any nitrogen oxides into nitrogen gas.[5, 6] Absorbent traps are then used to remove any remaining contaminants. Detection of gasses is done in a variety of different ways, such as gas chromatography, infra-red thermal conductivity cells, and chemical traps, but these depend on the detector used and the manufacturer from which the device is purchased.

In the literature, there are three main cases in which CHNS analysis is used to characterize CNMs. The first such case is when proving acid hydrolysis using sulfuric acid. This method of characterization is particularly useful in this instance because residual sulfur groups from acid hydrolysis are easily identifiable on the output spectra. This procedure has been done by researchers attempting to prove acid hydrolysis of cellulose I with sulfuric acid,[7] acid hydrolysis of cellulose into glucose,[8] and to prove extraction of CNFs from eucalyptus kraft pulp.[9]

The second such case is when functionalizing or incorporating a nanocellulose-based material with a functional group or molecule. If the functionalized groups contain N or S this procedure is particularly simple as these groups are easily identified in the output spectra. If the groups contain only elements also contained within nanocellulose itself (C, O, or H), CHNS analysis can be used for this as output CHNS spectra will show an increased peak for that element. However, although CHNS analysis can be used to prove C, O, and H bond modification, XPS is preferred for that particular situation as the modified C's in the sample can be identified more exclusively. Researchers have used CHNS to verify the degree of substitution of cetyl trimethylammonium bromide modified CNC,[10] degree of bisphosphonate modification of phosphonated nanocellulose,[11] verify aminosilane functionalization of CNCs,[12] peptide incorporation levels on CNCs from cotton,[13] glycidyl trimethyl ammonium chloride modified CNFs,[14] amination of a microfibrillated cellulose,[15] verification of poly(propylene carbonate)-coatings on nanofibrillated cellulose glycerol,[16] and azo dye adsorption onto the surface of microcrystalline cellulose.[17]

The third case is when attempting to measure the degree of chemical leeching in polymers containing CNMs when the leachate contains C, H, N, S, or O, such as when investigating organic chemical leaching outside of polymer solutions.[18] However, CHNS analysis cannot be run on a liquid sample, thus the sample must be dried beforehand.

While this method of analysis is highly quantitative in nature, it does have its limitations. The working range of CHNS analysis of C- or N- containing samples is generally accepted as above 0.05% by weight (500 ppm) among researchers, although some tools advertise values less than this[19-21]. Within the working range the uncertainty is 200-300ppm[19, 20, 22]; thus, one must be careful using CHNS analysis at low loading levels. Samples containing phosphorous can also suffer from systematic deviations in the determined carbon content exceeding the tolerance limits advertised on many tools[22]. It is difficult to characterize differences in C, O, or H content before and after chemical modification due to the large background signal from cellulose structure in CNMs. Due to chemical limitations of this EA technique, it is not useful for characterization of any element other than C, H, N, S, O and sometimes halogens in a CNM-containing sample.

Secondary Ion Mass Spectrometry (SIMS) and Time of Flight SIMS (ToF-SIMS)

SIMS chemical analysis is a method through which the surface of a material is characterized by being bombarded by a focused primary ion beam, typically argon ions (Ar^+), gallium ions (Ga^+) or alkali metal ions.[23] Primary ions sputter the surface and cause secondary ions from the surface of the material to be ejected into the atmosphere above the material. These secondary ions are then filtered into a mass spectrometer and are analyzed. SIMS detectors in this regard are limited in sampling depth to around 1-2 nm.[23] The most commonly used mass spectrometer detector used for organic molecules is time of flight (ToF) as one can obtain the full mass spectrum in one operation rather than having to scan through a full mass spectrum in one operation.[23]

There are three main modes of SIMS analysis: 1) static SIMS, 2) scanning SIMS, and 3) dynamic SIMS. In static SIMS, the surface is sputtered in the same location and the chemical composition of the material can be measured from the surface to a depth of around 1 nm.[23] Static SIMS is usually used to determine whether the composition of a material is changing with depth and can be used to determine the intermediate steps in a catalyzed reaction. Static SIMS is done to a depth of 1.5nm and a spatial resolution of 200nm.[24] However, with static SIMS quantification can be difficult. Scanning SIMS, in which the surface of a material is sputtered to a short depth but is scanned across a wide area, can also be performed to characterize if there are any chemical concentration differences along the surface of a material or to determine if there are any surface contamination and thin layer structures.[25] The spatial resolution is dependent upon the primary beam size, but can be anywhere in the range of 0.5-3μm.[26] The third method, dynamic SIMS, uses a very high beam intensity to cut the sample through a very fast sputtering technique. This allows you to measure the composition as a function of the depth of the material, but unlike in static SIMS this permanently damages the material.[23]

In literature, ToF-SIMS has been used to verify the presence of chemical modification and lateral amino acid distribution in amino acid modified cellulose surfaces and as confirmation of the presence of individual amino acids on the fibrous networks of cellulose after chemical coupling.[27] Other researchers have used this method for verification of fatty acyl chain modification in modified CNMs. This was done by looking for characteristic peaks associated with the acyl chain-derived ions, which was used to indicate that fatty acids had been attached by covalent bonds to the fiber matrix.[28] Other researchers have used ToF-SIMS to verify the surface modification of CNFs through acetylation in an ionic liquid.[29] In any case, the main application of SIMS in nanocellulose characterization is in verification of chemical modification.

From the literature, it is clear that time-of-flight secondary ion mass spectroscopy characterization has been used when characterizing CNMs for qualitative analysis of the presence of chemical functionalization on the surface of the CNMs. Because SIMS is a highly surface sensitive analysis technique (with sampling depths limited to the first atomic layers),[23] it is used in this application for the verification of surface chemical modification. However, ToF SIMS is limited due to the fact that its output is not easily quantifiable in nature, thus another EA method must be used to quantify results, such as XPS or CHNS.

X-ray Photoelectron Spectroscopy (XPS) and Auger Electron Spectroscopy (AES)

XPS, also known as electron spectroscopy for chemical analysis (ESCA), is a chemical analysis method in which the surface of a material is irradiated with x-rays. Core shell electrons in the atoms on the surface are energized from these x-rays and escape from their atoms and become photoelectrons.[30] Core shell electrons in specific atoms in specific energy shells have specific, defined energies associated with them. The associated energy of emitted ions can therefore be used to characterize the composition of a material.[31] AES works very similar to XPS, but is based on the Auger theory in which the energy of a core shell electron entering a hole left by an escaping photoelectron is able to emit energetic electrons from the same atom known as Auger electrons.[32] These Auger electrons can be used to characterize the chemical composition of the material due to their characteristic energies. For the purposes of this analysis either method could be used for the characterization described in each source in this section, but as XPS has been used more in the context of cellulosic nanomaterials, the discussion will focus on that technique.

XPS has been used to characterize CNMs for two main reasons. First is to provide quantitative analysis of the carbon linkages to prove chemical modification on the surface of modified CNMs. This technique has proven chemical modification of PET fabrics with CNC particles,[32] bromine and sulfur in modified CNC samples,[33] carbon bond modification for esterification of CNCs,[34] and modification of CNCs for ATRP,[35] and to characterize oxygen and carbon content in CNFs.[36] XPS is also useful for characterization of heavier ions such as iron[37] and to characterize the oxidation state of metal nanoparticles in solutions containing CNMs.[38]

XPS and AES do have associated limitations. First, the sample must be solid. Second, they lack sensitivity for trace chemical identification. Third, the results one obtains for the material are only for the surface, not the bulk. Thus, in order to use XPS/AES to characterize a material one must assume the surface properties are indicative of the bulk material, which is not the case in every application. Another major consideration when performing these surface sensitive techniques is that of carbon contamination, which is present on nearly all surfaces exposed to the atmosphere. On cellulosic samples there is often a significant amount of C1 contamination (from 5-7% error) in output spectra.[39] The error is often even higher and less predictable in samples that have come in contact with other materials such as plastics, cellophane film, aluminum, and/or glass.[39] Thus, care in sample handling must be taken. It is also recommended that for reproducible data of cellulose that only low-power monochromatic irradiation be used.[39] Nevertheless, XPS is particularly useful when determining relative changes of non-carbon elements on the surface of a CNM.[40] While XPS and AES are quantitative by nature, the data are dependent upon sample handling/preparation to limit contamination, integrating all elements present, proper calibration of electron yield and work function, beam damage of the sample, and charge compensation. Thus it is advised to consider results relative to results obtained at the same time on the same instrument and not compare to results found in literature or on a different XPS analyzer, unless one is sure that proper methodologies were followed.[40]

Energy Dispersive X-ray Spectroscopy (EDS or EDX)

EDS is an analytical technique where a high-energy beam of charged particles or an x-ray is used to characterize a sample. Atoms within the sample contain ground-state electrons in discrete energy levels bound to the nucleus which, when excited by an outside source, can be ejected from their shells creating an electron hole. An electron from an outer shell can then fill this hole, releasing an x-ray with energy equal to the energy difference between the outer-shell and inner-shell.[41] The number and energy of these x-rays is measured by an energy-dispersive spectrometer and is used to characterize the sample.

EDS is a particularly useful EA method for the characterization of CNMs because it is often attached to SEM devices. Because of this, one can easily obtain chemical composition of surfaces that are visually identified on the SEM. EDS has been used for quantitative measurement of chemical composition of metal nanoparticle-nanocellulose hybrid composites,[38] for characterizing CNF-containing copper nanoparticles,[42] characterizing S and N composition on S,N-doped graphene-modified nanocellulose,[43] for quantitative analysis of chemical composition on polypyrrole-nanocellulose composites,[44] for quantification of calcium and phosphorous content in bacterial nanocellulose scaffolds,[45] and for semi-quantitative EA of bacterial nanocellulose reinforced fiber-cement composites.[46] In every instance listed above, EDS was used in conjunction with SEM analysis.

EDS does have some limitations. It is difficult to characterize light elements with this characterization method, although researchers have used EDX to characterize C, O, and S content in sugarcane-sourced CNMs.[47] In this particular instance SIMS, XPS, and CHNS EA would be more applicable. Second, EDS lacks the sensitivity required to perform trace chemical identification and thus cannot be used for characterization of very small amounts of atoms.

Inductively Coupled Plasma (ICP) Mass Spectrometry and Atomic Emission Spectroscopy

Inductively coupled plasma (ICP) is a technique that uses a plasma to ionize atoms within the sample so they can be analyzed subsequently by mass spectrometry or atomic emission spectroscopy. Free electrons are introduced to an Argon gas stream inside a magnetic field. Electrons interact with the magnetic field and oscillate back and forth, colliding with gaseous atoms and releasing electrons which are then accelerated producing a fireball that consists mainly of argon atoms with a small fraction of free electrons and argon ions.[48] The sample to be studied enters the ICP, evaporates and causes constituent atoms to ionize. At high temperatures within the plasma, a significant proportion of the atoms become ionized, each atom losing its most loosely bound electron to form an ion with a single positive charge.[49] These ions are then extracted through a series of cones into a mass spectrometer and are separated on the basis of their mass-to-charge ratio. Alternatively, ICP-atomic emission spectroscopy (ICP-AES) can be used where the excited plasma photoemission is analyzed for characteristic frequencies and is similar to atomic adsorption and glow discharge spectroscopies. Both detection methods (MS or AES) are functionally equivalent in that the elemental composition is analyzed. Hence, we will refer to the technique as ICP-MS/AES

ICP-MS/AES is useful for characterization of CNMs when considering medium to heavy weight atoms in CNM-containing composites. The main application of this characterization method in the identification of metallic or salt compounds or impurities in a CNC sample. One group measured the amount of zirconia in their sample, as their milling process included the use of zirconia milling balls.[50] ICP-AES has been used to characterize palladium leaching in Pd nanoparticles supported onto bacterial CNFs[51] and for verification of Pd loading in CNC-catalyzed Heck coupling reactions.[52] ICP-AES analysis has also been used for characterization of Ca/P ratios for HA-CNC composite systems for biomimetic bone scaffolds.[53]

ICP-MS/AES is a powerful method of EA, but cannot be used for characterization of light elements. Further, due to hesitation of many scientists to inject solids or samples in which solids are dispersed into the instrument, ICP-MS/AES is often only performed on liquid samples. However, it is ideal for leachate analysis after ultrafiltration or centrifugation to remove the CNM.

Bibliography

1. Thompson, M., CHNS Elemental Analysers AMC Technical Briefs 2008, 29, 1-2.
2. Steyermark, A., Microdetermination of Sulfur. In Quantitative Organic Microanalysis, 2 ed.; Academic Press Inc.: New York, NY, 1961; pp 276-315.
3. Steyermark, A., Microdetermination of Oxygen. In Quantitative Organic Microanalysis, 2 ed.; Academic Press Inc.: New York, NY, 1961; pp 377-409.
4. Steyermark, A., Microdetermination of Halogens. In Quantitative Organic Microanalysis, 2 ed.; Academic Press Inc.: New York, NY, 1961; pp 316-353.
5. Steyermark, A., Microdetermination of Nitrogen by the Dumas Method. In Quantitative Organic Microanalysis, 2 ed.; Academic Press Inc.: New York, NY, 1961; pp 151-187.
6. Thompson, M., CHNS Elemental Analysers. The Royal Society of Chemistry 2008, 1-2.
7. Neto, W.; Putaux, J.; Mariano, M.; Ogawa, Y.; Otaguro, H.; Pasquini, D.; Dufresne, A., Comprehensive morphological and structural investigation of cellulose I and II nanocrystals prepared by sulphuric acid hydrolysis. Rsc Advances 2016, 6 (79), 76017-76027.

8. Pang, J.; Wang, A.; Zheng, M.; Zhang, T., Hydrolysis of cellulose into glucose over carbons sulfonated at elevated temperatures. Chemical Communications 2010, 46 (37), 6935-6937.
9. Tonoli, G.; Teixeira, E.; Correa, A.; Marconcini, J.; Caixeta, L.; Pereira-da-Silva, M.; Mattoso, L., Cellulose micro/nanofibres from Eucalyptus kraft pulp: Preparation and properties. Carbohydrate Polymers 2012, 89 (1), 80-88.
10. Zainuddin, N.; Ahmad, I.; Kargarzadeh, H.; Ramli, S., Hydrophobic kenaf nanocrystalline cellulose for the binding of curcumin. Carbohydrate Polymers 2017, 163, 261-269.
11. Sirvio, J.; Hasa, T.; Ahola, J.; Liimatainen, H.; Niinimaki, J.; Hormi, O., Phosphonated nanocelluloses from sequential oxidative-reductive treatment-Physicochemical characteristics and thermal properties. Carbohydrate Polymers 2015, 133, 524-532.
12. Mohd, N.; Ismail, N.; Zahari, J.; Fathilah, W.; Kargarzadeh, H.; Ramli, S.; Ahmad, I.; Yarmo, M.; Othaman, R., Effect of Aminosilane Modification on Nanocrystalline Cellulose Propertiesq. Journal of Nanomaterials 2016.
13. Edwards, J.; Prevost, N.; Sethumadhavan, K.; Ullah, A.; Condon, B., Peptide conjugated cellulose nanocrystals with sensitive human neutrophil elastase sensor activity. Cellulose 2013, 20 (3), 1223-1235.
14. Pahimanolis, N.; Salminen, A.; Penttila, P.; Korhonen, J.; Johansson, L.; Ruokolainen, J.; Serimaa, R.; Seppala, J., Nanofibrillated cellulose/carboxymethyl cellulose composite with improved wet strength. Cellulose 2013, 20 (3), 1459-1468.
15. Meng, Y.; Young, T.; Liu, P.; Contescu, C.; Huang, B.; Wang, S., Ultralight carbon aerogel from nanocellulose as a highly selective oil absorption material. Cellulose 2015, 22 (1), 435-447.
16. Spoljaric, S.; Salminen, A.; Luong, N.; Seppala, J., Ductile nanocellulose-based films with high stretchability and tear resistance. European Polymer Journal 2015, 69, 328-340.
17. Garcia-Amoros, J.; Bucinskas, A.; Reig, M.; Nonell, S.; Velasco, D., Fastest molecular photochromic switches based on nanosecond isomerizing benzothiazolium azophenolic salts. Journal of Materials Chemistry C 2014, 2 (3), 474-480.
18. Takegawa, A.; Murakami, M.; Kaneko, Y.; Kadokawa, J., A Facile Preparation of Composites Composed of Cellulose and Polymeric Ionic Liquids by In situ Polymerization of Ionic Liquids having Acrylate Groups. Polymer Composites 2009, 30 (12), 1837-1841.
19. 2400 Series II CHNS/O User Manual. PerkinElmer, Ed. 2011; pp 1-12.
20. Carbon, Hydrogen, and Nitrogen Determination using the PerkinElmer 2400 Series II CHNS/O Analyzer. PerkinElmer, Ed. 2011.
21. Bance, S., Handbook of Practical Organic Microanalysis. Michrochemical Journal 1980, 15, 590-597.
22. Elemental CHNS Analysis. https://www.univie.ac.at/Mikrolabor/CHNS_eng.htm (accessed September 27).
23. Griffiths, J., Secondary ion mass spectrometry. Analytical Chemistry 2008, 80 (19), 7194-7197.
24. Time-of-Flight Secondary Ion Mass Spectrometry (TOF-SIMS). (accessed September 26).

25. Gritsch, M.; Brunner, C.; Piplits, K.; Hutter, H.; Wilhartitz, P.; Schintlmeister, A.; Martinz, H., Application of scanning SIMS techniques for the evaluation of the oxidation behavior of high-purity molybdenum. Fresenius Journal of Analytical Chemistry 1999, 365 (1-3), 188-194.

26. Kota, N. In SIMS Basics, HiRes2017, University of Wisconsin- Madison, University of Wisconsin- Madison, 2017.

27. Kalaskar, D.; Ulijn, R.; Gough, J.; Alexander, M.; Scurr, D.; Sampson, W.; Eichhorn, S., Characterisation of amino acid modified cellulose surfaces using ToF-SIMS and XPS. Cellulose 2010, 17 (4), 747-756.

28. Freire, C.; Silvestre, A.; Neto, C.; Gandini, A.; Fardim, P.; Holmbom, B., Surface characterization by XPS, contact angle measurements and ToF-SIMS of cellulose fibers partially esterified with fatty acids. Journal of Colloid and Interface Science 2006, 301 (1), 205-209.

29. Missoum, K.; Belgacem, M.; Barnes, J.; Brochier-Salon, M.; Bras, J., Nanofibrillated cellulose surface grafting in ionic liquid. Soft Matter 2012, 8 (32), 8338-8349.

30. Briggs, D., Handbook of X-Ray and Ultraviolet Photoelectron Spectroscopy. Heyden & Son: London, 1977.

31. SIEGBAHN, K., ELECTRON-SPECTROSCOPY FOR ATOMS, MOLECULES AND CONDENSED MATTER. Uspekhi Fizicheskikh Nauk 1982, 138 (2), 223-248.

32. Li, W.; Ding, E., Characterization of pet fabrics surface modified by graft cellulose nano-crystal using TGA, FE-SEM and XPS. Surface Review and Letters 2006, 13 (6), 819-823.

33. Boujemaoui, A.; Mongkhontreerat, S.; Malmstrom, E.; Carlmark, A., Preparation and characterization of functionalized cellulose nanocrystals. Carbohydrate Polymers 2015, 115, 457-464.

34. Tian, C.; Fu, S.; Habibi, Y.; Lucia, L., Polymerization Topochemistry of Cellulose Nanocrystals: A Function of Surface Dehydration Control. Langmuir 2014, 30 (48), 14670-14679.

35. Morandi, G.; Heath, L.; Thielemans, W., Cellulose Nanocrystals Grafted with Polystyrene Chains through Surface-Initiated Atom Transfer Radical Polymerization (SI-ATRP). Langmuir 2009, 25 (14), 8280-8286.

36. Huan, S.; Bai, L.; Liu, G.; Cheng, W.; Han, G., Electrospun nanofibrous composites of polystyrene and cellulose nanocrystals: manufacture and characterization. Rsc Advances 2015, 5 (63), 50756-50766.

37. Liu, S.; Liu, Y.; Deng, F.; Ma, M.; Bian, J., Comparison of the effects of microcrystalline cellulose and cellulose nanocrystals on Fe3O4/C nanocomposites. Rsc Advances 2015, 5 (91), 74198-74205.

38. Kaushik, M.; Moores, A., Review: nanocelluloses as versatile supports for metal nanoparticles and their applications in catalysis. Green Chemistry 2016, 18 (3), 622-637.

39. Johansson, L.-S.; Campbell, J. M., Reproducible XPS on biopolymers: cellulose studies. Surface and Interface Science 2004, 36, 1018-1022.

40. Reid, M. S.; Villalobos, M.; Cranston, E. D., Benchmarking Cellulose Nanocrystals: From the Laboratory to Industrial Production and Applications. Langmuir 2017, 33 (7), 1583–1598.

41. Newbury, D. E., Energy-Dispersive Spectrometry. In Characterization of Materials, John Wiley & Sons, Inc.: 2002.

42. Zhong, T.; Oporto, G.; Peng, Y.; Xie, X.; Gardner, D., Drying cellulose-based materials containing copper nanoparticles. Cellulose 2015, 22 (4), 2665-2681.

43. Ruiz-Palomero, C.; Soriano, M.; Benitez-Martinez, S.; Valcarcel, M., Photoluminescent sensing hydrogel platform based on the combination of nanocellulose and S,N-codoped graphene quantum dots. Sensors and Actuators B-Chemical 2017, 245, 946-953.

44. Hebeish, A.; Farag, S.; Sharaf, S.; Shaheen, T., Advancement in conductive cotton fabrics through in situ polymerization of polypyrrole-nanocellulose composites. Carbohydrate Polymers 2016, 151, 96-102.

45. Sundberg, J.; Gotherstrom, C.; Gatenholm, P., Biosynthesis and in vitro evaluation of macroporous mineralized bacterial nanocellulose scaffolds for bone tissue engineering. Bio-Medical Materials and Engineering 2015, 25 (1), 39-52.

46. Mohammadkazemi, F.; Doosthoseini, K.; Ganjian, E.; Azin, M., Manufacturing of bacterial nano-cellulose reinforced fiber-cement composites. Construction and Building Materials 2015, 101, 958-964.

47. Kumar, A.; Negi, Y. S.; Choudhary, V.; Bhardwaj, N. K., Characterization of Cellulose Nanocrystals Produced by Acid-Hydrolysis from Sugarcane Bagasse as Agro-Waste. Journal of Materials Physics and Chemistry 2014, 2 (1), 1-8.

48. HUANG, M.; HIEFTJE, G., SIMULTANEOUS MEASUREMENT OF SPATIALLY RESOLVED ELECTRON TEMPERATURES, ELECTRON NUMBER DENSITIES AND GAS TEMPERATURES BY LASER-LIGHT SCATTERING FROM THE ICP. Spectrochimica Acta Part B-Atomic Spectroscopy 1989, 44 (8), 739-749.

49. Jean-Michel, M., Fundamental Principles of Inductively Coupled Plasmas. In Inductively Coupled Plasma Spectrometry and its Applications, Hill, S. J., Ed. Blackwell Publishing Ltd: Plymouth, UK, 2007; pp 27-60.

50. Amin, K.; Annamalai, P.; Morrow, I.; Martin, D., Production of cellulose nanocrystals via a scalable mechanical method. Rsc Advances 2015, 5 (70), 57133-57140.

51. Cirtiu, C.; Dunlop-Briere, A.; Moores, A., Cellulose nanocrystallites as an efficient support for nanoparticles of palladium: application for catalytic hydrogenation and Heck coupling under mild conditions. Green Chemistry 2011, 13 (2), 288-291.

52. Shi, S.; Chen, S.; Zhang, X.; Shen, W.; Li, X.; Hu, W.; Wang, H., Biomimetic mineralization synthesis of calcium-deficient carbonate-containing hydroxyapatite in a three-dimensional network of bacterial cellulose. Journal of Chemical Technology and Biotechnology 2009, 84 (2), 285-290.

53. Yin, N.; Chen, S.; Ouyang, Y.; Tang, L.; Yang, J.; Wang, H., Biomimetic mineralization synthesis of hydroxyapatite bacterial cellulose nanocomposites. Progress in Natural Science-Materials International 2011, 21 (6), 472-477.

APPENDIX F. REVIEW OF DRINKING WATER QUALITY IMPACTS OF SPRAY-ON PLASTIC LININGS

This work was prepared as a collaborative work with researchers in Civil and Environemntal and Ecological Engineering. For this work I am listed as second author and wrote the "material properties of interest and characterization" section. Additionally I assisted in reformatting and re-writing a large portion of the document throughout. This work will be submitted at a future date.

ABSTRACT

This review was conducted to better understand chemical leaching from popular polymer-based pipe linings including epoxy, polyurethane, and polyurea thermosetting systems. Results showed that few publicly available drinking water quality impact studies have been conducted for epoxy lining products on U.S. epoxy products, only one study was found for polyurethane, and no studies were found for polyurea. The limited data available show wide ranges in water quality impacts caused across and within lining products. Studies have reported organic carbon contributions of up to 345 mg/L, continued leaching after six months of installation, water pH reductions by 1-2 pH units, disinfectant loss, disinfectant byproduct (DBP) production, odor, and microbial growth. Contaminants are ingredients and byproducts of lining manufacture. Some contaminants have health-based drinking water standards. A battery of studies should be commissioned to examine how formulations and installation practices influence chemical leaching so drinking water quality can be predicted at the tap.

KEYWORDS: Lining, rehabilitation, epoxy, plastic, leaching

INTRODUCTION

In the U.S., about 1 million miles of public drinking water pipes are in use, and private drinking water plumbing is estimated to number more than 6 million miles (Nguyen, Elfland, & Edwards, 2012). Since the 1970s, plastic pipes have become popular for drinking water conveyance. Before plastic pipes were available, metal (i.e., steel, cast iron, ductile iron and copper) and concrete were the predominant materials used for buried water distribution systems and service lines (American Water Works Service Company, 2002; Lytle & Nadagouda, 2010). Many of these existing pipes have deteriorated and surpassed their predicted 50-100 year service-life. Pipe aging can lead to biofilm growth, chemical leaching, scaling, and aesthetic problems, and sometimes these conditions can pose health risks to consumers (National Research Council, 2006). For example, lead leaching from lead service lines has been linked to elevated blood lead levels in children (Hanna-Attisha, LaChance, Sadler, & Schnepp, 2016; Jean Brown, Raymond, Homa, Kennedy, & Sinks, 2011). Replacement of buried drinking water pipes would cost an estimated $1 trillion (ASCE Committee on America’s Infrastructure, 2017).

Spray-on polymer linings are a common trenchless technology for pipe repair, preventative maintenance, and corrosion mitigation. More than 20 years ago, epoxy resin systems were proposed to reduce lead leaching from building plumbing on military installations and prior to that had been used for U.S. aircraft carrier piping systems (USN, 1999). Conventional pipe replacement (e.g., lead service line replacement) requires excavation and can cause public disruption including roadway shutdowns and temporary water shutoffs. To avoid these consequences, in-situ trenchless pipe repair technologies are used to repair damaged or harmful pipes in place. Epoxy, polyurethane, and polyurea resin systems are sprayed onto the inner pipe wall, creating a barrier between the drinking water and deteriorated host pipe (AWWA, 2001). This process is quick: reportedly, an epoxy lining can be installed within 12-16 hr, and polyurethane and polyurea linings can be installed in 30 min (AWWA, 2001).

Before additional discussion about water pipe repairs is provided, it is important to note that the words “coatings” and “linings” have been used interchangeably in the American drinking water industry literature, and the definitions used for this study are described below. A commonly cited drinking water contact material leaching procedure defines “linings” as “prefabricated materials applied, bonded, or attached to a surface that is subject to direct/indirect contact with drinking water” (NSF International, 2016). ASTM F3182 defines “linings” as the material bonded to host pipe interior diameter (ASTM, 2016). Interestingly, the drinking water contact leaching procedure defines “coatings” too. A coating is “a material applied to a surface where a direct bond to the substrate is formed” (NSF International, 2016). For this definition however, drinking water is not specifically mentioned. In addition, potable water product manufacturers have used the word “lining” for the interior of pipe and coating for the pipe’s exterior (Northwest Pipe Company, 2015). In the present review study, linings are defined as plastic material bonded to the host substrate that contact drinking water.

It is difficult to estimate how often spray-on linings are used. Several manufacturers produce similar products, and while applied in public works, this information is not collectively reported, to the best of the authors' knowledge. The global coatings raw material market is estimated to be valued at $63.5 billion and currently 34.3 metric tons of coatings materials are estimated to be in use today (Pilcher, 2018). Installation success is often based on mechanical performance alone, and the rate of success, while likely high, is difficult to estimate. Neither industry nor installers publicly disclose information about failed installations. While there have been several reports of successful application of epoxy, polyurethane, and polyurea linings to water pipelines in and outside the U.S. (Deb, Snyder, Hammel, and Tyler, 2006), failures have also been reported (Dromgool, 2013).

Lining failures can be grouped into several categories including (1) installation based failure (when installers in the field fail to properly clean the host pipe, do not adhere to instructions, ingredients are defective, and linings are not properly manufactured), (2) degradation failure (mechanical failure with aging that reduces the estimated lifetime), and (3) water quality failure (when linings introduce unacceptable water quality changes). While some of these failures become critical (i.e., pipe breakage), many more likely go unnoticed. As an example of an inadequate pipe cleaning installation failure, dust entrainment in a new lining led to higher lead drinking water levels (USN, 1999). A non-critical failure falling into all 3 categories is demonstrated in **Figure 1** with unevenly distributed linings(a) and broken epoxy linings(b) related to a 7 year old pipe rehabilitation project. The unevenness is not intended by manufacturers, the broken epoxy is due in part to aging, and the flakes contribute negatively to water quality. A glue-like odor was also detected for these degraded linings.

Since these linings are expected to have 20+ year service-lives, their impact on drinking water quality is a topic worth scrutiny. Their potential to (i) release contaminants with primary maximum contaminant levels, (ii) cause off-tastes and -odors, (iii) contribute to microbial growth, (iv) enable disinfectant byproduct (DBP) generation, and (v) alter water pH should be considered. With long service lives, the impact of aging pipes is also noteworthy, but is difficult to study.

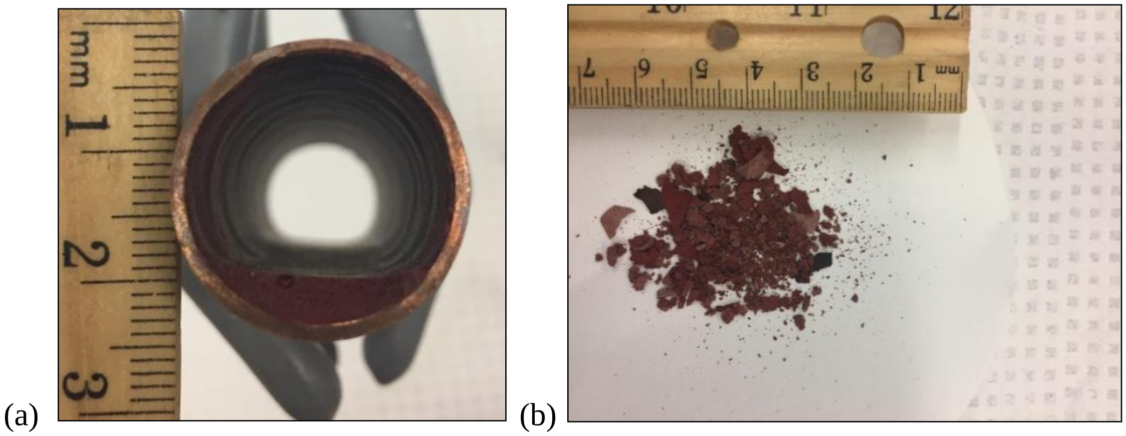

Figure 7.4 (a) Uneven wall thickness of epoxy in a copper hot water plumbing pipe (b) and pieces of the lining found in the faucet aerator. These were found in a 7 year old rehabilitated plumbing pipe in California.

This review was conducted to better understand chemical leaching from popular polymer-based pipe linings and their impact on drinking water quality. Specifically, we investigated how these linings are formed in the field, properties of the different materials used in these linings, standards to regulate quality, and leaching literature. Investigating materials properties together with leachate properties allows for a complete understanding of drinking water quality impacts, as summarized in our conceptual model (**Figure 2**). Throughout the review, we emphasize failures and maximum concentrations (i.e., the worst case scenario). This is for several reasons including: (1) unpublished data for passing, certified projects is not available; (2) reporting bias emphasizes the compounds that are found over those that are not; and (3) maximum concentrations are relevant for acute exposure toxicity to compounds. Finally, we recommend future research steps.

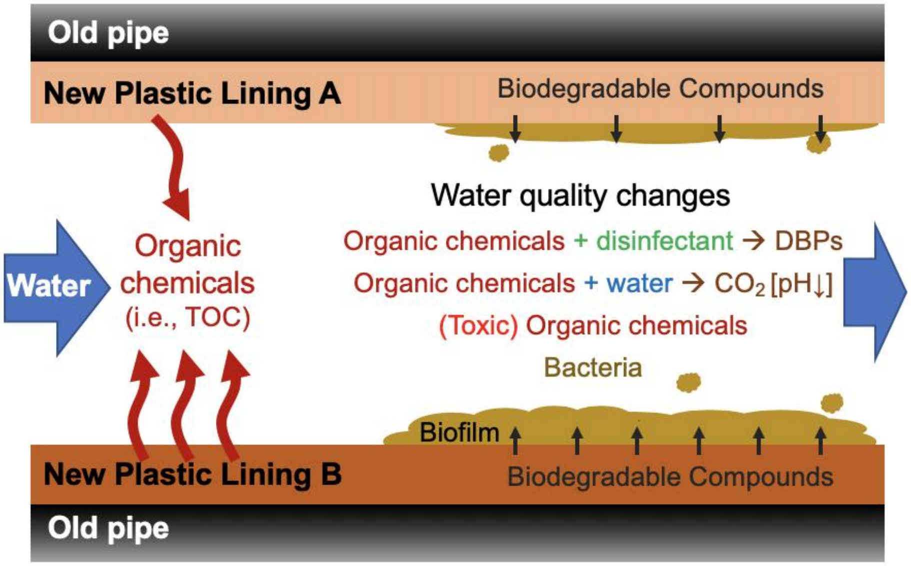

Figure 2: Expected drinking water quality impacts with new polymer linings. Polymer properties affect the leaching of organic chemicals (i.e., total organic carbon, TOC), which in turn affects the chemical and biological water quality. Organic chemicals can contribute to bacterial growth, the formation of disinfectant by-products (DBPs), water chemistry changes (pH), and health, as some organic chemicals have toxicity.

MATERIAL FORMATION

The linings used most often in the potable water industry, listed in ASTM F1216 and F1743, are epoxy, polyurea and polyurethane; however, many others are used in sanitary sewer systems including vinyl ester, polyester and phenolic coatings (ASTM, 2003, 2012). The materials used in pipe linings are thermoset materials, which consist of two precursor chemicals – a resin and a hardening agent – which, when mixed and heated, react to produce a material with a molecular-level crosslink network (Callister, 1985). This process, referred to as "curing," is irreversible and results in a material with higher mechanical, thermal, and chemical properties than either precursor chemical alone (Callister, 1985). However, while many individuals colloquially consider only the precursor resin and hardener when studying linings in this application, it is also important to consider the variety of compounds added into these systems to enhance the properties of the thermoset. These chemical additives can be accelerators (also known as catalysts, promoters, initiators, and dryers), toughening agents, flame retardants, thinning agents, stabilizers, coloring agents, and even other materials like glass fiber and metals (Burton, 2013; Fei et al., 2017; Knight, 1999; Muralisrinivasan, 2013; Visakh, 2015). These chemicals and additives alone can constitute up to 80% of the weight and/or volume of the resulting thermoset polymer depending on the desired properties of the material (Muralisrinivasan, 2013). Many of these chemical additives have synergistic effects with each other and can further improve the resulting material properties to be better than either chemical alone: this is particularly prominent for flame retardant additives (Döring, Ciesielski, & Heinzmann, 2012). It is also important to consider that while adding these compounds can have desirable effects on the properties of the thermoset system prior to crosslinking, they remain in the resulting cured thermoset and can have deleterious effects on the lining's properties after crosslinking. For example, the addition of only 5% weight of a thinning agent can decrease the compressive strength of the resulting thermoset up to 35%, increase the time needed to achieve acceptable cure, change the color of the resulting material, and cause shrinking and cracking (Knight, 1999).

While ideally one would expect thermoset polymers to fully react in situ, this is not the case in practice (i.e., installation based failure). Previous researchers have shown a significant portion of the resin and hardener in epoxy systems remain unreacted in the crosslinked thermoset (Li, Xiao, Moon, & Wong, 2006), and oligomers are also present. There is also not a consistent degree of crosslinking in polymer systems across the volume of the thermoset, which creates particular areas of the system that can be more susceptible to degradation. Over several years, these unreacted components can leach into the water supply leaving behind voids which weaken the overall thermoset itself (i.e., degradation failure and water quality failure) (Li, Xiao, Moon, & Wong, 2006). Curing for longer amounts of time can help decrease the presence of these unreacted monomer units, but removing them completely from the resin is impossible without the aid of chemical accelerants (Li, Xiao, Moon, & Wong, 2006). Additionally, curing for too long can result in oxidative aging related damage, prematurely aging the pipe.

For all linings, the process of application in the field is described in (Randtke et al., 2017) and includes 1) roughening, 2) cleaning and drying, and then 3) lining the surface. Linings better adhere to rough surfaces than smooth ones. For this reason, the surface to be lined is roughened in the field using a sand-blaster. Next, the surface is flushed with tap water to remove any dust and then dried using heated, filtered air. The lining material is then flowed into the pipe as air is simultaneously pressurized, creating a vortex which forces the lining material to flow through the pipe while it is spun onto the wall. This pressure is held for 2-3 hours to ensure an even lining, expedite curing, and minimize pooling. In **Figure 3**, one can see the process of ‘spinning’ the materials onto a transparent pipe. Care must be taken to prepare pre-polymer material mixtures with the appropriate viscosity such that they will flow easy enough to evenly line the surface of the pipe without flowing too easily and completely escaping the pipe once air is blown through it.

Figure 3: Application of epoxy resin (red) onto a clear pipe. The epoxy resin is essentially ‘spun’ onto the pipe wall using a vortex of air pressure. Photo courtesy of Zachary A. Breault, University of Kansas.

MATERIAL PROPERTIES OF INTEREST AND CHARACTERIZATION

When considering materials appropriate for particular linings and the potential for various failures, the properties most often considered are the glass transition temperature (T_g), the heat deflection temperature (HDT), and the thermal degradation temperature (T_d) (**Table 1**). The glass transition temperature is the temperature at which the atoms in a sample of polymer have enough thermal energy to vibrate out of their lowest energy “locked-in” state and become able to move (Callister, 1985). At a macro scale, polymers above their T_g will still appear stiff, but their elastic modulus will significantly decrease (i.e., by up to 90% as compared to below the T_g) (Korey, Mendis, Youngblood, & Howarter, 2018). The T_g is important in lining applications because linings are meant to be used below their T_g. When the service temperature of the lining is greater than the material’s T_g, the linings can become soft and tacky. This can lead linings to becoming more susceptible to particulate accumulation, permeation, and decreased adhesion, impact resistance, and hardness. Thermoset materials that regularly cycle above their T_g have decreased maximum mechanical stiffness below the T_g (Ehrler, 2005). Using a thermoset regularly above its T_g will result in decreased liner service-life (Ehrler, 2005). Thus, when choosing a material, it is important to confirm the T_g is significantly higher than the temperature at which the material will be routinely used.

Table 1. List of Material Property and Characterization Acronyms

Acronym	Description
HDT	Heat deflection temperature
T_g	Glass-transition temperature
T_d	Thermal degradation temperature
TGA	Thermogravimetic analysis
TMA	Thermomechanical analysis
DMA	Dynamic mechanical analysis
DSC	Differential scanning calorimetry

Typical T_gs for thermoset materials have a wide range, which is why they are so useful for a variety of different applications. However, for the linings industry most linings have been found to have serviceable temperatures between room temperature and 100°C (180°F) (EpoxyTec, 2018; Envirocort Technologies, 2015). The T_g is impacted by a variety of factors including, but not limited to, the structure of the polymer's main chain, the degree of inter-chain bonding determined by vinyl groups off of the main chain, and the amount of free volume in the polymer (Callister, 1985). The T_g can be measured using a multitude of characterization methods, but the most often used are thermomechanical analysis (TMA) for applications where load is applied in a non-cyclical manner, dynamic mechanical analysis (DMA) for applications where a cyclical load is applied, and differential scanning calorimetry (DSC) for all applications (Turi, 1981). Most researchers will perform either TMA or DMA, but not both; however, most researchers will also run DSC on their samples to verify the result from either TMA or DMA (Turi, 1981). From DMA and TMA, the T_g that is reported and marketed is usually the maximum of the tan(δ) curve, but it is important to also consider the breadth of the tan(δ) curve as the material will have softened to some extent before the maximum tan(δ) is observed. When considering T_g, it is important to remember that DMA, TMA, and DSC determine this value through different mechanisms and often slightly disagree with each other even when the same heating rate is used. Using the lower of the two results is suggested when determining whether a thermoset could be used in a specific lining application.

The HDT – also known as deflection temperature under load (DTUL) or the heat distortion temperature – is the temperature at which a polymer deforms a specified distance under a specified load. It is dependent on the load applied and the deformation distance determined by the measurement. Unlike T_g, which, HDT is a metric dependent upon the characterization method. HDT is most often industrially measured using the apparatus specified in ASTM D648 or ISO 75 (ASTM, 2018; McKeen, 2014). However, TMA and DMA can also be used to measure the HDT. While it is not recommended to use the HDT test alone for product design, the HDT can be a more targeted measurement than T_g for a particular application. This is because as long as the required load is known for the lining (e.g. water pressure in a pipe) and the tolerance of the part is known, one can very easily determine the usable temperature range for a particular lining. Typical heat deflection temperatures for epoxy and polyurethane/polyurea linings are between 100-150˚C, although this value is largely determined by the applied load and the addition of chemical additives into the thermoset (McKeen, 2014; Zeus Industrial Inc., 2005).

The T_d is also an important measurement for determining whether a particular lining or lining is appropriate for an application, especially in high temperature pipe linings. The T_d of a sample is the temperature at which a material begins to thermally degrade in the resulting application (McKeen, 2014). For thermoset polymers such as epoxy and polyurethane/polyurea, this temperature is often in the range of 300-800˚C and is a function of the monomer units being used, the crosslinking temperature, and any chemical additives added into the system. T_d is measured using thermogravimetic analysis (TGA). The temperature of thermal degradation is often recorded as the maximum point of the derivative weight curve, but can also be reported as the temperature at which thermal degradation is initiated on the derivative weight curve (McKeen, 2014). For design purposes, it is suggested to consider the temperature of initiation of thermal degradation to avoid any amount of material degradation in the pipe.

EPOXY

Epoxy linings are produced from the polymerization of two components, a resin and hardener. Epoxy resin, which is typically a prepolymer, typically contains bisphenol A diglycidyl ether (BADGE) or bisphenol F diglycidyl ether (BFDGE), which have epoxy groups at each end (**Figure**

4); however, many other commercially available epoxy resins are multi-epoxy functional and contain three or more groups (Ratna, 2009). These chemicals are often chemically formed as the result of the chemical reaction between precursor chemicals such as bisphenol A (BPA) or bisphenol F (BPF) and epichlorohydrin, which results in mono or bi-glycidylated monomers (Ratna, 2009). Novolac glycidyl ether (NOGE) is another prominent resin for commercial use (Xue, Wan, & Kannan, 2016). The hardener is described as a curing agent and multi-functional amines are often used (Wicks, Jones, Pappas, & Wicks, 2007) due to their high degree of reactivity and ability to crosslink quickly at low temperatures; however, other hardening agents are used industrially in other applications including sulfur, phenolic (novolac), and even bio-based hardening agents (Korey, Mendis, Youngblood, & Howarter, 2018). As mentioned previously, manufacturers will also add other compounds into epoxy formulations, with different manufacturers preferring to add different compounds. For example, volatile components, known as thinning agents (e.g., methanol and isopropanol) are usually added because they can reduce epoxy resin viscosity to assist with epoxy application and they evaporate at the high curing temperatures used (Knight, 1999). Other additives include catalysts and stabilizers (Wicks, Jones, Pappas, & Wicks, 2007). Epoxy linings are cured at temperatures from room temperature up to 200 $_o$C. The choice of resin and hardening agents, the weight ratio of each added to the system, and the addition of chemical accelerators or other additives has a significant impact on the temperature required for crosslinking (Burton, 2013). The resulting T_g of the thermoset is often 10-20°C above the crosslinking temperature (Carbas, Marques, Silva, & Lopes, 2014). Epoxy linings take several hours to fully install (at least 2-3 hours cure time), but can be less expensive than the more quickly installed polyurethane or polyurea linings (Oram, 2004; Randtke et al., 2017).

Epoxy hardening agents and resins are added in varying weight ratios depending on the specific resin and hardener being added. However, the properties of the resulting polymers are often best when a 1 to 1 molar ratio of the epoxy groups on the resin to the reactive groups on the hardener is used. An excess of reactive groups of resin or hardener results in unreacted molecules in the crosslinked thermoset, a decrease in the local crosslinking density of the system, and a decrease in overall properties of the crosslinked thermoset. While the mix ratio is typically provided by the supplier, the hardener is often between 10 wt% and 50 wt% of the final mix, but this is dependent on the molecular structure of both precursor chemicals (Liu et al., 2015).

Due to concerns with lining service-life, research has been performed on the hydrolytic degradation of epoxy thermosets. In the case of epoxy, the natural occurrence of hydroxyl and hydronium ions present in water can facilitate degradation of the ether bonds (Cohen & Van Aartsen, 1973; Le Gac, Choquese, & Merlot, 2013; Liu, Li, Songquan, & Yuting, 2012). Once bond degradation occurs, the network loosens and the molecular chains become more available for further hydrolytic degradation. This could result in network depolymerization under extreme conditions (Liu, Li, Songquan, & Yuting, 2012). Degradation products include ketones and other aromatic compounds. When BADGE is used as the resin precursor, research suggests that at high temperature this can result in the release of bisphenol A (Liu, Li, Songquan, & Yuting, 2012). It should be noted that degradation rates are highly variable, and depend on a number of factors. Although a service life of 40 to 60 years has been estimated, the authors of that same study found epoxy linings to be in poor condition after a service life of as little as 3 years (Deb, Snyder, Hammel, and Tyler, 2006).

POLYURETHANE/POLYUREA

Polyurethane and polyurea synthesis reactions are shown in **Figure 4**. Isocyanate is the common prepolymer material for both polyurethane and polyurea linings. When this component reacts with a polyol, which has hydroxyl groups at each end and works as the hardener, a polyurethane is formed. When isocyanate is polymerized with a polyamine, a polyurea is formed. Varying the length, chemical structure, or the number of hydroxyl or amine groups on the polyol or the polyamine can affect the resulting properties of the thermoset (Oprea, 2013; Tan, Jia, Sheng, Liu, & Yang, 2012).

The main difference between polyurea and polyurethane is that polyurea systems have a more rapid reaction time (typically less than 30 seconds) and are able to crosslink without a catalyst. Polyurethane systems require catalysts (Citadel Floors, 2017). Polyurea systems are often significantly more expensive than polyurethane systems (Citadel Floors, 2017). For this reason, polyurethane/polyurea blend linings have been used to obtain the low temperature crosslinking of the polyurea, but reduce the cost overall (American Water Works Association, 2001; Citadel Floors, 2017). Some polyurethane and polyurea linings have been reported to be free of volatile organic carbon (VOC) or “VOC-free” (Deb, McCammon, Snyder, & Dietrich, 2010; Najafi, 2010), so leaching of solvents is reportedly lower than prior generation linings.

In the case of polyurethane, polyurea, or polyurethane/polyurea blend linings, the natural occurrence of hydroxyl and hydronium ions present in water leads to degradation of the ester and/or amide bonds in the sample (Cohen & Van Aartsen, 1973; Le Gac, Choquese, & Merlot, 2013; Liu, Li, Songquan, & Yuting, 2012). As in the case in epoxy, once bond degradation occurs, the local network becomes loosened, increasing the availability of additional ester and/or amide bonds for further hydrolytic degradation, and the final result is a depolymerization of the network (Liu, Li, Songquan, & Yuting, 2012), which releases monomers into the aqueous media. In the case of linings for water pipes, monomer selection is important to ensure release of non-toxic monomer units into the water supply as these thermoset networks undergo hydrolytic degradation.

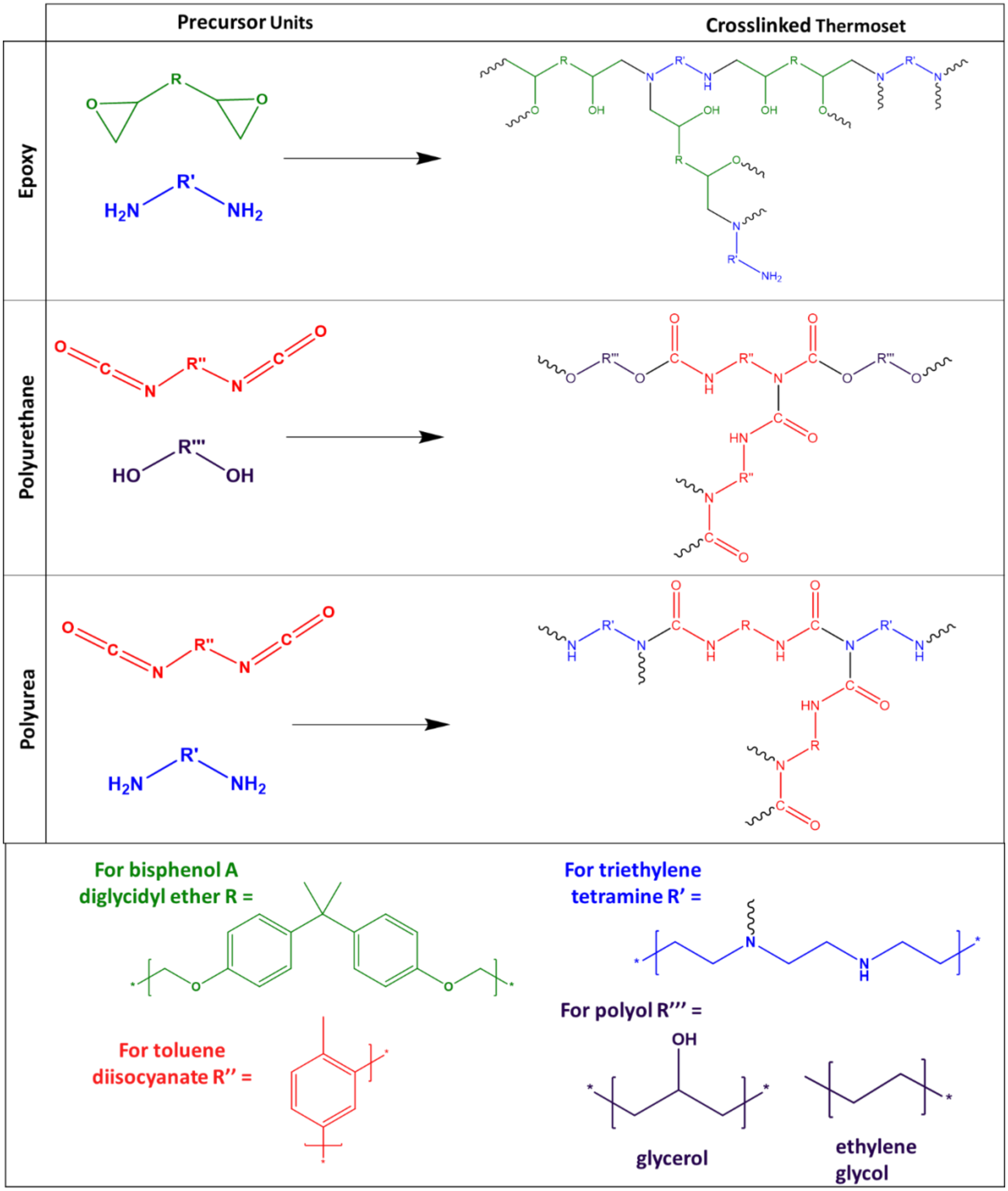

Figure 4 Synthesis scheme for epoxy, polyurethane, and polyurea.

STANDARDS AND TEST PROTOCOLS FOR MECHANICAL FAILURE

The relevant standards and test protocols for mechanical failure that were found are listed in **Table 2**. ASTM F3182 describes lining requirements for the thickness verification test, liner bonding test, and immersion test (ASTM, 2016). The liner thickness should meet or exceed 1 mm or the minimum thickness specified by the manufacturer. To test the liner's bond to the host pipe, the tensile adhesion test, adhesion test, and tape test are recommended.

AWWA standard C210 is for liquid-epoxy coating systems and applies to the interior and exterior of steel water pipe and fittings. To determine an epoxy's chemical resistance, an immersion test is required. In this standard, 50 mm × 150 mm × 3.2 mm steel panels are coated and then soaked in three types of solutions (deionized water, 1 wt% sulfuric acid solution, 1 wt% sodium hydroxide solution) at 24°C for 30 days. Blistering, peeling, or disbandment of the lining is considered a failure (AWWA, 2008a).

To evaluate a polyurethane lining's chemical resistance, an immersion test is conducted in accordance with AWWA standard C222 (a standard for polyurethane coatings for the interior and exterior of steel water pipe and fittings). As part of this test, the lining weight and dimension values are measured after complete immersion at a minimum temperature of 21°C for 30 days (AWWA, 2008b). Samples (40 mm × 125 mm) are prepared, should not be attached to any substrate, and at least four immersion solutions should be used: 10% sulfuric acid, 30% sodium chloride, 30% sodium hydroxide and #2 diesel fuel. A sample that passes the test has less than a 5% change of weight and less than 5% change of dimension after immersion. Also, blistering, cracking, softening or other forms of deterioration after 24 hr immersion is considered not acceptable (AWWA, 2008b).

Table 2. Standards and test protocols for spray-on plastic lining

Standard	Name	Epoxy	Polyurethane	Polyurea
ASTM F3182	Standard Practice for the Application of Spray-Applied Polymeric Liners Inside Pipelines for Potable Water	√	√	√
AWWA C222	Polyurethane Coatings for the Interior and Exterior of Steel Water Pipe and Fittings	-	√	-
AWWA C210	Liquid-Epoxy Coating Systems for the Interior and Exterior of Steel Water Pipelines	√	-	-
AWWA M28	Rehabilitation of Water Mains	√	√	√

Check mark represents the standard is suitable for the type of material, dash represents the material is not mentioned in the standard.

THE STANDARD 61 TEST

The only practice found for evaluating water quality impacts of tank and pipe linings in the U.S. is the NSF International Standard 61 procedure (NSF International, 2016) (**Table 3**). Test samples are prepared in accordance with the manufacturer's instructions. Each sample is conditioned with disinfectant immediately following curing. After conditioning, the sample is either exposed to test water immediately or dried in a laminar flow hood (air flowrate not specified) for a maximum of 4 hr before exposure to test water. The test temperature is selected according to the lining system's application (23 °C: cold water application; 60 °C: domestic hot water application; 82 °C: commercial hot water application). During the exposure, the water is periodically discarded and replaced. For pipe liners, water is left in contact with the material for 16 hr before collection; for tank liners, a water sample is collected after 24 hr.

The declared intent of the Standard 61 procedure is to determine if contaminants released from the lining materials to drinking water (under certain conditions) are within acceptable limits. For the Standard 61 procedure, water samples are analyzed for individual organic compounds. For epoxy, the compounds that may be analyzed include BPA, BPF, epichlorohydrin, BADGE, BFDGE, bisphenol A-propoxylate, bisphenol F-propoxylate, a variety of solvents, reactive diluent additives, and VOCs. Testing is often conducted by the NSF International itself, and their test results are not made publicly available. If, according to the procedure, formulation information indicates that any of these compounds are not present, NSF International may waive the testing for those chemicals. For polyurethane linings, VOCs are required to be analyzed. Polyurea was not mentioned in the Standard 61 procedure. The first Standard 61 certified epoxy lining material was approved in 1995 and AWWA standard for epoxy lining was issued in 2008 (AWWA, 2001).

Table 3 Standard 61 testing procedure found for different applications

Extraction procedure	**Pipe and related product**	**Tank products**
Time between curing and disinfection conditioning	Immediately	Immediately
Disinfection conditioning	50 mg/l free chlorine, 3 hr	200 mg/l free chlorine, 0.5 hr
Time between disinfection conditioning and testing	Immediately, maximum 4 hr	Immediately, maximum 4 hr
Exposure water quality	Hardness 100 mg/l; pH 8.0; 23, 60 or 82 °C	

Table 3 continued

Exposure water conditioning	16 (14) days	4 (0) days
Time between water sample analysis and exposure water conditioning	16 hr	24 hr

In brackets, the time periods are for lining systems intended for immediate return to service. Immediate return to service lining systems are intended to return service within 48 hr after curing.

EPOXY DRINKING WATER IMPACTS

In the 1970s, epoxy lining technologies were introduced in the U.K. for drinking water pipelines. Between 1982-1988, epoxy linings in the U.K. had variable quality: for example, some resin/hardener mixing ratios were incorrect (Deb, McCammon, Snyder, & Dietrich, 2010). Concerns about epoxy lining impacts on drinking water quality and the lack of experience in the U.S. delayed the application of this technology for drinking water pipelines (Deb, Hasit, & Norris, 1999). The first U.S. epoxy lining site test found for a drinking water pipe was conducted in 1993 (Conroy, Hughes, & Wilson, 1995). Chester Water Authority (Pa.) provided a test site, and one 80-year-old 168 m long unlined cast iron dead end 150 mm water main was lined. A water flowing test was conducted for 30 days and water samples were collected on days 1, 3, 7 and 30. Water quality was compared against National Primary Drinking Water Regulations, but the water quality analysis methods applied were not mentioned. No difference in total trihalomethane (TTHM) concentration (chloroform and bromodichloromethane) for epoxy lined pipes was found compared with the adjacent unlined water pipes. Other organic compounds were detected and the highest concentration was 4 µg/L, however, the names of those organic compounds were not reported.

Very few studies have been conducted to understand drinking water quality impacts of epoxy lined pipes or tanks (**Table 4**). For the U.S., only five studies were found. These examined a total of 10 epoxy drinking water lining material formulations over the past 27 years. The scope and depth of these studies is limited. A 2017 analysis of epoxy formulations concluded that "since epoxy formulations, application methods, curing times and other factors vary among manufacturers, the results are not necessarily representative of those that would be obtained using other epoxy formulations or application methods" (Randtke et al., 2017). Thus, utilities, regulators, and health officials lack enough information to make decisions about epoxy leaching across formulations, contractors, and applications. Although materials are tested with standards (described above), these do not account for application based failures or degradation failures that can lead to water quality failures.

Available U.S. epoxy studies have shown that organic chemicals can leach from new and old epoxy linings, some chemicals can react with disinfectants, DBPs can be formed, odor can be caused, and microbial growth can occur (**Table 4**). Total organic carbon (TOC) is a general indicator of organic contaminants present and it has been employed to determine if organic compounds are released from epoxy to water. Since 2002, four studies have reported organic carbon leaching results for nine epoxy formulations. The typical TOC level in drinking water can range from 0.5-8 mg/L (van der Wielen and van der Kooij, 2010), but in a City of Calgary study, one epoxy formulation caused a TOC increase up to 345 mg/L (Satchwill, 2002). It should be noted that this study was not peer-reviewed and the surface area to volume ratio was not reported. However, TOC increase above the background has been noted in a peer reviewed study (Heim & Dietrich, 2007). Compounds that contribute to TOC may or may not have primary maximum contaminant levels (MCL) or cause undesirable effects (i.e., off-tastes and -odors, microbial growth, alter pH). Epoxy linings have been shown to cause water odor (Deb, McCammon, Snyder, & Dietrich, 2010; Heim & Dietrich, 2007). Odor problems occurred regardless of the presence of disinfectant. “Plastic”, “chemical” and “sweet” were the common descriptors and odor persisted during one 30-day study (Deb, McCammon, Snyder, & Dietrich, 2010).

Table 4 U.S. and Canada Epoxy Drinking Water Applications

Year	Epoxy Test Condition	Water Quality Impacts
2017 (Randtke et al., 2017)	1 NSFI approved formulation	1. BADGE ranged from 13-340 µg/L
	Water type: lab prepared water (pH 8, 6.5)	2. BADGE, BFDGE hydrolyzed and decayed
	Disinfectant: Free chlorine, Monochloramine	3. BPA, BPF did not decay
	Temperature: 20-25 °C	4. BPA, BPF, and triethylenetetramine (TETA) reacted with both disinfectants
	Duration: 10 days	5. BADGE did not react with disinfectants
2010 (Deb, McCammon, Snyder, & Dietrich, 2010)	1 NSFI approved formulation (new)	1. TOC 6.3 mg/L (day 1), 1.7 mg/L (day 30)
	Water type: lab prepared water (pH 8)	2. BPA 33 µg/L (day 1), trace (day 30)
	Disinfectant: Free chlorine, Monochloramine	3. Odor described as “plastic/ chemical/ sweet”
	Temperature: 19-23 °C	4. Disinfectant loss occurred
	Duration: 30 days	5. DBPs were produced (THM <60 µg/L & HAA5< 80 µg/L)
	1 NSFI approved formulation (5 years old)	1. TOC 3.5 mg/L
	Water type: lab prepared water (pH 8)	2. Disinfectant loss occurred
	Disinfectant: Free chlorine	3. DBPs were produced (HAA5 < 12 µg/L)
	Temperature: 19-23 °C	4. Microbial growth occurred
	Duration: 30 days	
2007 (Heim & Dietrich, 2007)	1 formulation	1. TOC 0.6 mg/L
	Water type: lab prepared water (pH 7.7-7.9)	2. Odor described as "plastic/adhesive/putty"
	Disinfectant: Free chlorine, Monochloramine	3. BPA; phenol, nonyl-phenol, styrene, toluene, benzaldehyde
	Room temperature	4. DBPs were produced (3–9 µg/LTHM)
	Duration: several months	
2002 (Satchwill, 2002)	5 NSFI approved formulations	1. Total BTEX ranged from 0.2 to 48 mg/L
	Water type not reported	2. TOC ranged from 34 to 345 mg/L
	Temperature: 49 °C	3. Pre-rinsing had little effect on leaching
	Duration: 72 hr	4. Extended dry times had limited impact on reducing leaching
1989 (Alben, Bruchet, & Shpir, 1989)	1 formulation in lab; 3 field storage tanks	1. MIBK, *o*-, *m*-, *p*-xylene; ethoxy ethyl acetate; methyl benzaldehyde
	Water type: lab prepared water (pH 8.5)	2. Disinfectant loss occurred
	Disinfectant: Free chlorine	3. DBPs may have been produced
	Temperature: 23 °C	4. Water soaking caused more rapid leaching than air drying
	Duration: 4 weeks	5. MIBK and xylenes detected in two of the three tanks

Individual organic contaminants have been detected and measured in some U.S. studies. Organic compounds (17) were found in water that contacted epoxy lining, including raw materials of monomer synthesis (e.g. BPA), monomers (e.g., BADGE), solvents (e.g., methyl isobutylketone [MIBK], benzene, toluene, ethylbenzene, and xylenes [BTEX]), and additives (e.g., nonyl-phenol). BPA was only analyzed in 3 studies, but was found as high as 33 µg/L in the first 24 hours (Deb, McCammon, Snyder, & Dietrich, 2010). BADGE was detected in 9 of 36 samples (with all positives having hold-times less than 24 hours) and the highest concentration was of 340 µg/L (Randtke et al., 2017). MIBK and xylenes were detected at up to 378 and 183 µg/L respectively (Alben, Bruchet, & Shpir, 1989), and BTEX leached up to 48 mg/L (Satchwill, 2002).

Epoxy linings have also been shown to exert a free chlorine and monochloramine disinfectant demand. Prior testing conditions included disinfectant level (2-3 mg Cl_2/L), temperature (19-25 °C) and pH (7.7-8.0). Randtke et al., (2017) investigated free chlorine consumption of 18 new epoxy linings applied to copper and lead pipes, and observed that most free chlorine (>90%) was consumed in the first 6 hr, with a consumption rate of approximately 25.3 mg as Cl_2/m_2-day in this period. Deb et al. (2010) examined disinfectant consumption of a new epoxy lining and a five years old epoxy lining with a 30-day test with sporadic chlorinated water replacement. The new lining was not conditioned before water exposure. For the new lining, consumption rate of both free chlorine (40.6 mg as Cl_2/m_2-day) and monochloramine (48.2 mg as Cl_2/m_2-day) was fastest in the first 24 hr, and decreased by one order of magnitude over the 30 days testing. For the old lining, only free chlorine was tested, and the consumption rate was consistently ~50 mg Cl_2/m_2-day over the 30-day test. Another study tested a new epoxy lining in chlorinated and chloraminated water for "3-4" days (Heim & Dietrich, 2007). The new lining was conditioned with 50 mg/L free chlorine for 3 hr before testing, and the consumption rate of the lining was 1.8-2.7 as mg Cl_2/m_2-day for free chlorine and 1.2-1.6 as mg Cl_2/m_2-day for monochloramine. The results from these studies implied that epoxy linings' consumption rate of the two types of disinfectant are similar, and that disinfectant demand is long-lasting, with both new and aged epoxy exhibiting high free chlorine demand. Conditioning with disinfectant may reduce demand, as disinfectant conditioned epoxy lining showed a lower consumption than the linings that were not conditioned. At present, not all of the factors that can affect disinfectant demand of epoxy are known, and it is unclear if and when epoxy linings would no longer affect disinfectant residual.

When epoxy is in contact with disinfectants, DBPs can be formed. Four epoxy lining tests were found with disinfectants in the U.S, and all reported DBP formation, including THMs, five regulated haloacetic acids (HAA5) and other chlorinated compounds. Heim and Dietrich (2007) found more THMs produced in chlorinated water than in chloraminated water, and chloroform concentration increased to 60 µg/L when the epoxy leachate was treated with free chlorine for 3 hours. Alben et al., (1989) found more than 20 aromatic and unidentified compounds in 1mg/L chlorinated water exposed to epoxy. For the 200 mg/L chlorine dose, more than 20 aromatic and unidentified compounds were also found and some seemed to be similar to those in the low chlorine dose experiment (i.e., m-xylene, p-xylene, o-xylene, 3-chloro-4-methyl-2-pentanone, 3,3-dichloro-4-methyl-2-penatanone, bromochloro-xylene).

Seven published studies describing epoxy leaching into drinking water were found from outside the U.S. and Canada (**Table 5**). Similar water quality impacts were found, including organics leaching, disinfectant loss, DBPs formation and microbial growth. Three studies evaluated drinking water quality impacts by epoxy linings in the field, and detected organic compounds related to epoxy linings include BPA, BPF, 4-nonylphenol (4-NP), 4-*tert*-octylphenol, trichlorophenol (TCP), 2,4,6-trichloroanisole, 4-*tert*-butyl phenol (4-TBP), halogenated 4-TBP. Other organic compounds caused by epoxy leaching were reported: benzyl alcohol, monoglycidyle ether of butane diol, diglycidyl ether of butane diol, diaminodiphenylmethane, phthalates, benzaldehyde, ketones, and antioxidants (Bruchet, Elyasmino, Decottignies, & Noyon, 2014; Jackson, Warren, & James, 2007; Rajasärkkä et al., 2016).

The presence of organic compounds in water, coupled with disinfectant loss likely creates favorable conditions for microbial growth. One U.S study found that microbial growth occurred at the surface of a 5 year old epoxy lining (Deb, McCammon, Snyder, & Dietrich, 2010). While there is limited data about the bioavailability of the organic compounds found, the introduction of any organic compound to drinking water, which is designed to be carbon growth limited, likely promotes growth (Prest, Hammes, van Loosdrecht, & Vrouwenvelder, 2016). Most polymeric pipes have been shown to promote growth through the introduction of assimilable organic carbon (Bucheli-Witschel, Kötzsch, Darr, Widler, & Egli, 2012; van der Kooij & Veenendaal, 2001; Wen, Kötzsch, Vital, Egli, & Ma, 2015), and epoxy resin in other applications (Pangallo et al., 2015) and several of the organic compounds already identified (Sharma et al., 2009) are known to be biodegradable. Several countries require testing of linings' biological impact on drinking water quality (e.g., (German Environmental Agency (Umwelt Bundesamt), 2016), with a suggested limit of ≤1000 pg adenosine tri-phosphate (ATP)/cm$_2$). To the authors' knowledge, there is no publicly available data about the biological impact of epoxy linings. However, evidence suggests that linings release some bioavailable compounds. Epoxy resin used in other applications (Pangallo et al., 2015) and several of the organic compounds already identified (Sharma et al., 2009) are known to be biodegradable.

For epoxy linings, BPA has become a well-associated compound, and BPA's presence in drinking water has received some scrutiny. Globally, 8 of 12 published studies found regarding epoxy drinking water pipe linings examined drinking water for BPA. Since the testing conditions varied greatly across these studies (e.g., surface area/volume ratio, immersion time), BPA levels were normalized for the purposes of this discussion (µg/m$_2$-day) (**Table 6**). Rajasärkkä et al., (2016) found BPA leaching in the field up to 23.5 µg/L, but the pipe diameter was not reported so the normalized BPA leaching rate could not be determined. Across all studies found, BPA leaching varied significantly (0 to 6,936 µg/m$_2$-day). At 19-25 °C, BPA leaching rates ranged from 0.90 to 838 µg/m$_2$-day. Two Standard 61 approved epoxy lining formulation had reported leaching rates of 13.0 and 838 µg/m$_2$-day. The high normalized BPA leaching rates were most frequently found with short leaching durations (6 hr – 24 hr). BPA is known to be highly reactive with chlorine (Randtke et al., 2017), and in the presence of chlorine and with longer duration tests BPA concentrations will be lower. Thus, the products reported can still pass the NSF International 61 test which spans 14 days. However, short stagnation times are possible in these linings, and these high leaching rates are relevant when considering acute exposure to BPA.

Bench-scale and field-studies have shown that high water temperatures can cause greater leaching from epoxy linings (Bae, Jeong, & Lee, 2002; Rajasärkkä et al., 2016). For example, in Korea, the leaching rate increased by more than 200 times from 20 °C to 100 °C (Bae, Jeong, & Lee, 2002). In the U.S., the role of temperature on epoxy leaching has not been studied. BPA leaching changes over time have been studied in and outside the U.S. (Bruchet, Elyasmino, Decottignies, & Noyon, 2014; Deb, McCammon, Snyder, & Dietrich, 2010). Deb et al., (2010) found that BPA leaching decreased drastically from one NSF International approved epoxy after the first 24 hr, but was thereafter consistent. BPA leaching for new epoxies increased during a six month lab test in France (Bruchet, Elyasmino, Decottignies, & Noyon, 2014). In the field, it was discovered that 2 to 9 year old epoxy lined pipes were still capable of leaching a notable amount of BPA into drinking water (Rajasärkkä et al., 2016). Since only limited published data is available and there are many epoxy resin formulations on the market, it is difficult to predict the leaching behavior in application. Additional publicly available data are needed.

POLYURETHANE AND POLYUREA DRINKING WATER IMPACTS

Polyurethane and polyurea are rapid-setting polymers (AWWA, 2001). The first introduction of the rapid-setting polymeric lining, Copon Hycote 169, in the U.K. was conducted in 1999, potable water service return within the same day was achieved (Oram, Warren, & Gove, 2002). In the U.S., a trial project was conducted with Copon Hycote 169 in 2001. The lining material had the sealing capacity to prevent tetrachloroethylene (PCE) leaching from a vinyl lined asbestos cement pipe (Gove, Oram, & Mahoney, 2003).

Compared with epoxy lining studies, even fewer water quality impact studies have been conducted for polyurethane and polyurea linings. Only two published studies were found in the U.S (Deb, McCammon, Snyder, & Dietrich, 2010; Whelton, Salehi, Tabor, Donaldson, & Estaba, 2013). Deb et al., (2010) and Johnson (2008) evaluated polyurethane for drinking water applications. Odor, TOC increase, pH reduction, disinfectant loss, and DBP formation were found. “TOC was leached from polyurethane; however by day 15, the TOC leached decreased to background levels.” A consistent ~2 unit pH reduction occurred during the 30 day study. HAA5 (30 µg/L) was formed but THMs were not detected. Another chlorinated compound, chlorophenyl isocyanate, was detected but not quantified. “Pleasant” and “putrid” were used to describe the odor caused by polyurethane, and the highest FPA intensity rating was 8 over 30 days, but the smell was not related to these detected compounds. Whelton et al. (2013) examined chemical leaching for a new polyurea lining from a storm water pipe over 30 days at the bench-scale. The lining caused water pH to decrease by ~1 unit during the first 6 days at room temperature. The greatest increases of chemical oxygen demand (COD), TOC, and total nitrogen concentrations occurred in the first 3 days, and were 98.3 mg/L, 19.9 mg/L and 2.8 mg/L, respectively. Although microbial growth was not analyzed, five-day biochemical oxygen demand (BOD_5)/COD ratio of 0.1 was reported, indicating poor bioavailability for leaching compounds.

As with all polymeric pipes, the introduction of organic chemicals can influence growth in nutrient limited drinking water. Polyurethane is known to be biodegradable when used in other applications (Howard, 2002). Although poor bioavailability was shown for these linings in one study, many factors can affect this. Pipes with similar chemical compositions but different manufacturers, and thus likely different additives and manufacturing processes, have demonstrated variable contributions to microbial growth in the past (Proctor et al., 2016). Since polyurethane and polyurea linings introduce nitrogen to the system, exceedance of the secondary nitrogen nutrient limitations (Prest, Hammes, van Loosdrecht, & Vrouwenvelder, 2016), and nitrification (i.e., following introduction of urea groups (Howard, 2002)) are risks

Table 5 Epoxy studies from Outside the U.S. and Canada

Year	Epoxy Test Condition	Water Quality Impacts
2016, Finland (Rajasärkkä et al., 2016)	Six 2-9 years old linings in the field	1. BPF, 4-NP, 4-t-octylphenol rarely found; trace concentrations
		2. BPA was detected in the majority of samples; Maximum (cold water) 0.25 µg/L and (hot water) 23.5 µg/L
		3. Older epoxy leached 4-20x more BPA than newer epoxy
2014, France (Bruchet, Elyasmino, Decottignies, & Noyon, 2014)	3 linings	1. Epoxy #3 showed increasing leaching during 5 months
	Water type: mineral water (pH unknown)	2. BPA only found in absence of disinfectant, no BPF found at all
	Disinfectant	3. 2,4,6-trichlorophenol (TCP), a BPA chlorination by-product sporadically observed in the chlorinated water
	Temperature: 20 °C	4. Discontinuation of disinfectants enhanced leaching of BPA and TCP
	Duration: 6 months	
	27 old coated water tanks, 200 old coated pipe sections (10-20 years old)	1.TANKS: No BPA, BPF or TCP
		2. PIPES: High frequency of BPA and BPF detection, sometimes with maximum values around 1 µg/L; TCP and 2,4,6-trichloroanisole were found in a few samples

Table 5 continued

2012, Japan (Kosaka et al., 2012)	2 lining	1. Levels of BPA, chlorinated BPA increased in retained water
	Water type: tap water (pH unknown) and lab prepared water (7.0)	2. BPA leaching did not decrease during 24 months of continuous test
	Disinfectant: Chlorine (tap water only)	3. Sums of the levels of BPA and chlorinated BPA had a negative relationship with the residual chlorine levels
	Temperature: 23 °C	4. TCP was produced; 12 µg/L (24 months)
	Duration: 24 months	
2007, England (Jackson, Warren, & James, 2007)	Five 1-10 years old linings in the field	1. No detectable TOC
		2. GC-MS analysis found no epoxy specific compounds resulting from 4 epoxies
		3. One epoxy showed evidence of leaching of 4-t-butyl phenol (4-TBP), and the presence of halogenated 4-TBP products, with a max. 2.2 µg/L
2002, Spain (Romero, Ventura, & Gomez, 2002)	5 linings	1. BPA of 0.02-0.03 µg/cm^2
	Water type: ultrapure water	2. Benzyl alcohol of up to 180 µg/cm^2;
	Temperature: 40-45 °C	3. Phthalates of 0.04-0.3 µg/cm^2, benzaldehyde, 4-NP, ketones, antioxidants
	Duration: 5 days	
2002, Korea (Bae, Jeong, & Lee, 2002)	3 linings	1. BPA from unit area of epoxy resin lining was in the range of 10.68 to 1,734 µg/m^2
	Water type: DI water, lab prepared water (pH 7.0)	2. Higher risk of BPA leaching to drinking water during a summer season
	Temperature: 20, 50, 75, 100 °C	3. Microbial growth was higher with epoxy than in a stainless steel tank
	Duration: 6 hr (50-100 °C), 24 hr (20 °C)	
1999, France (Rigal & Danjou, 1999)	1 lining, 1 hr after installation (test conditions unknown)	1. Benzyl alcohol (345 µg/L), monoglycidyle ether of butane diol (12 µg/L), diglycidyl ether of butane diol (386 µg/L), diaminodiphenylmethane (72 µg/L), and a "series of derivatives from butanediol and diaminodiphenylmethane"
		2. Total flavor number: 6 "glue and bitter almond" to 2.5 "bitter flavor"

Table 6 Normalized Bisphenol-A BPA leaching rates from worldwide studies. Maximum BPA leaching rates were calculated using the maximum concentrations under reported testing conditions, the duration of the leaching test, and the surface area to volume (SA:V) ratio as needed.

Locations	**Epoxies tested, including ages***	**Testing conditions**						**Maximum BPA leaching**
		Water type	**Duration ****	**SA:V ratio *****	**Temperature**	**pH**	**Disinfectant**	**rate (µg/m^2-day)**
NSF/ANSI 61-2016	New lining materials	lab prepared	72 hr	50 cm^2/L min.	23, 60 or 82 °C	8.0	None	-
USA (Deb et al., 2010)	1 new Standard 61 approved formulation	lab prepared	24 hr	As 4” diameter pipe	19-23 °C	8.0	2 mg/L free chlorine; 4-6 mg/L monochloramine	838
France (Bruchet et al., 2014)	3 linings, (after 108 d use)	mineral	24 hr	50 cm^2/L	20 °C	NR	0.5 mg/L free chlorine; 0.25 mg/L chlorine dioxide	18.0
Japan (Kosaka et al., 2012)	1 lining (after 24 months use)	tap	16 hr	0.2 m^2/L	23 °C	NR	0.38-0.66 ppm free chlorine	0.975
	new lining prepared in lab	lab prepared		0.0546 m^2/L	23 °C	7.0	0	11.55
Korea (Bae et al., 2002)	3 new lining formulations	deionized & lab prepared	6 hr	reported per unit area	100 °C (50, 75 °C also tested)	7.0	none	6,936
			24 hr		20 °C			65
Spain (Romero et al., 2002)	5 new epoxy formulations	deionized	5 days	reported per unit area	40-45 °C	NR	0	60

NR represents not reported; *Total test time varied, age reported is the age at which the maximum concentration was found. “New” means the concentration was measured the first exposure water.

CONCLUSIONS

When assessing drinking water quality impacts of lining materials, it is critical to understand the lining’s properties and condition. Material properties can affect the product’s leaching behavior. For example, when considering the differences between Plastic A (less leaching) and Plastic B (more leaching) in **Figure 2**, there are many possibilities for the differences, including:

- Plastic A and B have the same formulation, but B has a lower T_g, allowing more leaching with the same water
- Plastic A and B have the same formulation, but due to installation differences one has more unreacted residual
- Plastic A and B are physically and chemically identical, but are exposed to environmental conditions (i.e., water quality, temperature)
- Plastic A raw materials that remain in the product and leach into water, are less reactive, biodegradable, or toxic than Plastic B
- Plastic B has undergone aging that resulted in depolymerization of the network

Since formulation (i.e., raw materials) vary between manufacturers or within one, and installation (i.e., cure times and temperatures) vary on every single installation, it is difficult to predict water quality impacts from these linings. Evidence from other pipe lining applications indicates that installers do not follow manufacturers' instructions on-site (Ra et al., 2019). With limited installation observations and few studies of products after on-site installation, it is difficult to determine if these variations are outliers or routine. Nonetheless, the limited existing studies have suggested that linings have the potential to negatively impact water quality. Evidence shows that polymer linings can leach organic chemicals into water, which increases organic carbon levels, reduces water pH, contributes to microbiological growth, and disinfectants may react with these materials. These reactions can reduce residual disinfectant concentration and generate DBPs. Some of the organic contaminants have health-based drinking water limits. Thus, further research is required to determine the extent of these impacts and strategies to limit the impacts in future applications.

RESEARCH NEEDS

To better understand lining water quality impacts, more publicly available bench-, pilot-, and field-scale testing data are needed. Currently data for only a few linings are available and testing conditions varied across published studies.

The focus for this review, and for much of the literature found, was on leaching behavior and solution-phase reactions. Additional reactions, like adsorption of organic contaminants in the water to the pipe, and diffusion of disinfectants into linings, may occur and should be studied.

To understand what individual chemicals can be leached from polymer linings, the chemical composition of resins and hardeners should be investigated. Various compounds have been found in the water associated with lining installations. For example, BPA has been found associated with epoxy lining (**Table 6**) and is used for epoxy resin production. However, the potential use and source of most of the compounds that have been reported have not been confirmed. Multiple analytical methods such as liquid chromatography-mass spectrometry (LC-MS), high performance liquid chromatography (HPLC), and gas chromatography-mass spectrometry (GC-MS), should be considered for future studies. In addition, it remains unclear which leached chemicals react with disinfectants, cause off-tastes and -odors, or contribute to microbial growth. Compounds leached from polyurea and polyurethane remain unidentified.

The factors that affect the amount of resin residual left in linings remains unclear and should be identified. Deb et al. (2010) reported that an incorrect resin/hardener ratio and inadequate curing can deteriorate water quality. In Finland, impacts of two pipe cleaning and preparation technologies on epoxy lining leaching revealed that the epoxy lined with the older technology leached more BPA than the epoxy lined with the later technology (Rajasärkkä et al., 2016). However, other factors including mixing process, cure time, lining thickness, and ratio of surface area to volume, may affect the observed chemicals, their concentrations, and their bioavailability, and should also be investigated. The extractable chemicals remaining in the linings after manufacture should be identified and how these differ across different installation conditions (e.g., mixing ratios, curing times, disinfectant doses, pH).

The impact of water quality and environmental conditions on polymer liner leaching should be investigated. Prior studies have used a variety test conditions to study leaching but published results did not enable the authors to predict water quality impacts. Previous results have shown that a higher water temperature can facilitate chemical leaching from epoxy (Bae, Jeong, & Lee, 2002), but the impact of other water parameters such as pH, mineral content, and water flow, and exposure duration remains unclear. Additional work is needed in this space.

The impact on biological stability of the water also requires further investigation. In addition to more thoroughly investigating the bioavailability of chemical leachate and its effect on total growth (i.e., by applying growth assays (van der Kooij & Veenendaal, 2001; Wen, Kötzsch, Vital, Egli, & Ma, 2015)), ecology must be considered. Pipe replacements in distribution networks are generally expected to have long-term effects on the biofilm community (Martiny, Jorgensen, Albrechtsen, Arvin, & Molin, 2003; Prest, Hammes, van Loosdrecht, & Vrouwenvelder, 2016). Spray-on linings would likely have similar affects, by offering a new surface for colonization and invasion. Since polymeric pipes have selective properties on the community present (Proctor et al., 2016; Rożej, Cydzik-Kwiatkowska, Kowalska, & Kowalski, 2015), care must be taken that these materials do not enrich an unwanted bacterial population (e.g., nitrification).

The bench-scale test procedures reviewed for this study often differed from one another, and many aspects are not included in the current Standard 61 procedure. For example, 1) The products are exposed to blowing air for 4 hr before Standard 61 testing, but available field studies do not report a similar pre-conditioning practice. 2) The test duration in published studies ranged from 3 days to several months. In Standard 61 procedure, water quality analysis is not conducted until pipe lining products are fully conditioned with air exposure and water exposure for 14 days, (i.e., no water sample is analyzed within the 14 days conditioning) (**Table 3**). 3) TOC increase and pH drop have been reported in prior studies, but TOC and pH measurements are not characterized for the post-leaching water. 4) The exposure water (100 mg/L hardness, pH 8, no disinfectant) in Standard 61 test is not representative of all or most drinking waters across the U.S and Canada. The impacts of exposure water contents on polymer leaching in drinking water system have been observed with other polymer products (Shotyk & Krachler, 2007). The role of the drinking water disinfectant is not considered in Standard 61, and DBP formation is not considered. 5) Organic leaching and disinfectant consumption may provide a friendly environment for microbial growth, but it is not addressed by Standard 61. 6) Off-tastes and -odors can be generated when new liners contact drinking water, sometimes prompting consumer concern, but aesthetic impacts are not considered in Standard 61. 7) The knowledge-gap between bench-, pilot-, and filed- scale tests is unclear. Two major limitations are that test results for Standard 61 approved products are not made public and testing does not represent field conditions. Until additional data become publicly available, the role of specific epoxy, polyurea, polyurethane linings on water quality will remain poorly understood.

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REFERENCES

Alben, K., Bruchet, A., & Shpir, E. (1989). *Leachate From Organic Coating Materials Used in Portable Water Distribution Systems*. *American Water Works Association*. Denver, CO.

American Water Works Service Company. (2002). American Water Works Company Completes Acquisition of Citizens Communications' Water and Wastewater Assets. In (pp. 1). New York.

ASCE Committee on America’s Infrastructure. (2017). *2017 American Infrastructure Report Card: Drinking Water*.

ASTM. (2003). Rehabilitation of Existing Pipelines and Conduits by Pulledin-Place Installation of Cured-in-Place Thermosetting Resin Pipe (CIPP). In (pp. 1-7).

ASTM. (2012). Rehabilitation of Existing Pipelines and Conduits by the Inversion and Curing of a Resin-Impregnated Tube). In (Vol. F1216, pp. 1-8).

ASTM. (2016) Standard Practice for the Application of Spray-Applied Polymeric Liners Inside Pipelines for Potable Water. ASTM International: West Conshohocken, PA, pp 1–6.

ASTM. (2018). Standard Test Method for Deflection Temperature of Plastics Under Flexural Load in the Edgewise Position. In (Vol. D648-18).

AWWA (American Water Works Association). (2001). *Rehabilitation of Water Mains - Manual of Water Supply Practices, M28 (3rd Edition)*; American Water Works Association: Denver, CO.

AWWA (American Water Works Association). (2008a). AWWA C210-07 Liquid-Epoxy Coating Systems for the Interior and Exterior of Steel Water Pipelines. American Water Works Association: Denver, CO, pp 1–28. https://doi.org/http://dx.doi.org/10.12999/AWWA.C210.07

AWWA (American Water Works Association). (2008b). AWWA C222-08 Polyurethane Coatings for the Interior and Exterior of Steel Water Pipe and Fittings. American Water Works Association: Denver, CO, pp 1–17. https://doi.org/http://dx.doi.org/10.12999/AWWA.C222.08

Bae, B., Jeong, J. H., & Lee, S. J. (2002). The quantification and characterization of endocrine disruptor bisphenol-A leaching from epoxy resin. *Water Science and Technology*, *46*(11–12), 381–387.

Bruchet, A., Elyasmino, N., Decottignies, V., & Noyon, N. (2014). Leaching of bisphenol A and F from new and old epoxy coatings: Laboratory and field studies. *Water Science and Technology: Water Supply*, *14*(3), 383–389. https://doi.org/10.2166/ws.2013.209

Bucheli-Witschel, M., Kötzsch, S., Darr, S., Widler, R., & Egli, T. (2012). A new method to assess the influence of migration from polymeric materials on the biostability of drinking water. *Water Research*, *46*(13), 4246–4260. https://doi.org/10.1016/j.watres.2012.05.008

Burton, B. L. (2013). *Acceleration of Amine-Cured Epoxy Resin Systems*. Paper presented at the Thermoset Resin Formulators Association, Newport, Rhode Island.

Callister, W. D. (1985). *Materials Science and Engineering* (9th edition, SI version.. ed.): Wiley Textbooks.

Carbas, R. J. C., Marques, E. A. S., Silva, L. F. M., & Lopes, A. M. (2014). Effect of Cure Temperature on the Glass Transition Temperature and Mechanical Properties of Epoxy Adhesives. *The Journal of Adhesion, 90*, 104-119. doi:10.1080/00218464.2013.779559

Citadel Floors. (2017) How Does Polyurea Measure Up to Other Coatings.

Cohen, J. L., & Van Aartsen, J. J. (1973). The hydrolytic degradation of polyurethanes. *Journal of Polymer Science: Polymer Symposia, 42*(3), 1325-1338. doi:10.1002/polc.5070420333

Conroy, P.; Hughes, D. M.; Wilson, I. (1995). *Demonstration of an Innovative Water Main Rehailitation Technique: In Situ Epoxy Lining*; AWWA Research Foundation: Denver, CO.

Deb, A. K.; Hasit, Y. J.; Norris, C. (1999). *Demonstration of Innovative Water Main Renewal Techniques*; AWWA Research Foundation: Denver, CO, 1999.

Deb, A., McCammon, S. B., Snyder, J., & Dietrich, A. (2010). *Impacts of Lining Materials on Water Quality [Project# 4036]*. Denver, CO USA.

Deb, A., Snyder, J., Hammel, J., Tyler, E. (2006) Service life analysis of water main epoxy lining. American Water Works Association Research Foundation (AWWARF).

Döring, M., Ciesielski, M., & Heinzmann, C. (2012). Synergistic flame retardant mixtures in epoxy resins. In (Vol. 1118, pp. 295-309).

Dromgool, M. B. (2013). *Epoxy Linings – Solvent Free But Not Problem Free*. Melbourne, Australia. Retrieved from www.epoxyproducts.com/solventfree.pdf

Ehrler, S. (2005). The compatibility of epoxy-based printed circuit boards with lead free assembly. *Circuit World, 31*(4), 3-13. doi:https://doi.org/10.1108/03056120510603080

Envirocort Technologies. *Poly-Triplex Cured in Place Manhole Liner.* (2015). Retrieved from Technical Data Sheet.

EpoxyTec. *CPP Sprayliner* (2018). Retrieved from Technical Data Sheet

Fei, X., Wei, W., Zhao, F., Zhu, Y., Luo, J., Chen, M., & Liu, X. (2017). Efficient toughening of epoxy-anhydride thermosets with a biobased tannic acid derivative. *Acs Sustainable Chemistry & Engineering, 5*(1), 596-603. doi:10.1021/acssuschemeng.6b01967

German Environmental Agency (Umwelt Bundesamt). 2016. “Recommendation: Guideline for Hygenic Assessment of Organic Coatings in Contact with Drinking Water (Coating Guideline).” https://www.umweltbundesamt.de/sites/default/files/medien/374/dokumente/97779_beschichtungsleitlinie_12238042_11_en_gepruft_final.pdf.

Gove, D. B.; Oram, P.; Mahoney, D. H. (2003). Relining Vinyl Lined AC Water Mains to Prevent PCE leaching—Sandwich, MA. *Pipelines*, 1012–1025

Hanna-Attisha, M., Lachance, J., Sadler, R. C., & Champney Schnepp, A. (2016). Elevated Blood Lead Levels in Children Associated With the Flint Drinking Water Crisis: A Spatial Analysis of Risk and Public Health Response. *American journal of public health, 106*(2), 283. doi:10.2105/AJPH.2015.303003

Heim, T. H., & Dietrich, A. M. (2007). Sensory aspects of drinking water in contact with epoxy lined copper pipe. *Water Science and Technology*, *55*(5), 161–168. https://doi.org/10.2166/wst.2007.175

Howard, G. T. (2002). Biodegradation of polyurethane: A review. In *International Biodeterioration and Biodegradation* (Vol. 49, pp. 245–252). Elsevier. https://doi.org/10.1016/S0964-8305(02)00051-3

Inoue, K., Sakamoto, T., Min, J., Todoroki, K., & Toyo'oka, T. (2014). Determination of dicyandiamide in infant formula by stable isotope dilution hydrophilic interaction liquid chromatography with tandem mass spectrometry. *Food Chemistry, 156*, 390-393. doi:10.1016/j.foodchem.2014.01.124

Jackson, P. J., Warren, I. C., & James, H. A. (2007). *The Long Term Migration of Substances from In-situ Applied Epoxy Resin Coatings*. Britten Road, Reading, UK.

Jean Brown, M.; Raymond, J.; Homa, D.; Kennedy, C.; Sinks, T. (2007). Association between Children’s Blood Lead Levels, Lead Service Lines, and Water Disinfection, Washington, DC, 1998-2006. *Environ. Res.*, *111* (1), 67–74. https://doi.org/10.1016/j.envres.2010.10.003

Johnson, H. (2008). Determination of the Influence of Polyurethane Lining on Potable Water Quality. June 2008. Thesis. Virginia Tech, Department of Civil and Environmental Engineering, Blacksburg, VA USA.

Knight, B. (1999). Thinning West System Epoxy. *Epoxyworks, 14*.

Korey, M., Mendis, G. P., Youngblood, J. P., & Howarter, J. A. (2018). Tannic acid: A sustainable crosslinking agent for high glass transition epoxy materials. *Journal of Polymer Science Part A: Polymer Chemistry, 56*(13), 1468-1480. doi:10.1002/pola.29028

Kosaka, K., Hayashida, T., Terasaki, M., Asami, M., Yamada, T., Itoh, M., & Akiba, M. (2012). Elution of bisphenol A and its chlorination by-products from lined pipes in water supply process. *Water Science and Technology: Water Supply*, *12*(6), 791–798. https://doi.org/10.2166/ws.2012.055

Le Gac, P. Y., Choqueuse, D., & Melot, D. (2013). Description and modeling of polyurethane hydrolysis used as thermal insulation in oil offshore conditions. *Polymer Testing, 32*(8), 1588-1593. doi:10.1016/j.polymertesting.2013.10.009

Li, Y., Xiao, F., Moon, K., & Wong, C. (2006). Novel curing agent for lead-free electronics: Amino acid. *Journal of Polymer Science Part a-Polymer Chemistry, 44*(2), 1020-1027. doi:10.1002/pola.21239

Liu, D., Zhao, W., Wu, F., Cen, Q., Zeng, Z., Wu, X., & Xue, Q. (2015). Effect of curing agent molecular structures on the tribological and corrosion behaviors of epoxy resin coatings. *Colloids and Surfaces A: Physicochemical and Engineering Aspects, 472*, 85-91. doi:10.1016/j.colsurfa.2015.02.036

Liu, Y., Li, L., Songquan, W., & Yuting, L. (2012). The Decomposition of Bisphenol A Diglycidyl Ether/Alicyclic Amine Hardened Networks in Near-critical Water. *Polymers & Polymer Composites*, *20*(9), 809-816.

Lytle, D. A., & Nadagouda, M. N. (2010). A comprehensive investigation of copper pitting corrosion in a drinking water distribution system. *Corrosion Science, 52*(6), 1927-1938. doi:10.1016/j.corsci.2010.02.013

Martiny, A. C., Jorgensen, T. M., Albrechtsen, H.-J., Arvin, E., & Molin, S. (2003). Long-Term Succession of Structure and Diversity of a Biofilm Formed in a Model Drinking Water Distribution System. *Applied and Environmental Microbiology*, *69*(11), 6899–6907. https://doi.org/10.1128/AEM.69.11.6899-6907.2003

McKeen, L. W. (2014). *The effect of temperature and other factors on plastics and elastomers* (3rd ed.. ed.): Waltham, Massachusetts ; Oxford, England : William Andrew.

Muralisrinivasan, N. S. (2013). *Plastics additives and testing*. Hoboken, New Jersey: Hoboken, New Jersey : John Wiley & Sons, Inc.

Najafi, M. (2010). *Trenchless Technology Piping: Installation and Inspection*; McGraw Hill Professional.

National Research Council. (2006). *Drinking Water Distribution Systems*. Washington, D.C.: National Academies Press. https://doi.org/10.17226/11728

Nguyen, C., Elfland, C., & Edwards, M. (2012). Impact of advanced water conservation features and new copper pipe on rapid chloramine decay and microbial regrowth. *Water Research, 46*(3). doi:10.1016/j.watres.2011.11.006

Northwest Pipe Company. (2015). Corrosion Control - Linings and Coatings. In (pp. 1-8). Vancouver, WA.

NSF International. (2016). NSF/ANSI 61 - 2016 Drinking Water System Components - Health Effects. NSF International: Ann arbor, MI 2016, pp 1–65.

Oprea, S. (2013). Effect of pyridazine content and crosslinker structure on the properties of polyurethane elastomers. *Journal of Applied Polymer Science, 128*(6), 3974-3981. doi:10.1002/app.38640

Oram, P.; Warren, I.; Gove, D. (2002). The Introduction And Implementation Of Rapid-Setting Polymeric Materials For In Situ Applied Linings (UK Experience). *Pipelines 2002: Beneath Our Feet: Challenges and Solutions*, pp 1–10.

Oram, P. (2004). Spray applied linings for water main rehabilitation: good or bad? New Orelans, North American Society for Trenchless Technology, NO-DIG.

Pangallo, D., Bučková, M., Kraková, L., Puškárová, A., Šaková, N., Grivalský, T., … Zemánková, M. (2015). Biodeterioration of epoxy resin: A microbial survey through culture-independent and culture-dependent approaches. *Environmental Microbiology*, *17*(2), 462–479. https://doi.org/10.1111/1462-2920.12523

Pilcher, G. R. (2018). The Demand for Coatings Raw Materials to 2022. *CoatingsTcech*, *14*(5).

Prest, E. I., Hammes, F., van Loosdrecht, M. C. M., & Vrouwenvelder, J. S. (2016). Biological Stability of Drinking Water: Controlling Factors, Methods, and Challenges. *Frontiers in Microbiology*, *7*, 45. https://doi.org/10.3389/fmicb.2016.00045

Proctor, C. R., Gächter, M., Kötzsch, S., Rölli, F., Sigrist, R., Walser, J.-C., & Hammes, F. (2016). Biofilms in shower hoses – choice of pipe material influences bacterial growth and communities. *Environ. Sci.: Water Res. Technol.*, *2*(4), 670–682. https://doi.org/10.1039/C6EW00016A

Rajasärkkä, J., Pernica, M., Kuta, J., Lašňák, J., Šimek, Z., & Bláha, L. (2016). Drinking water contaminants from epoxy resin-coated pipes: A field study. *Water Research*, *103*, 133–140. https://doi.org/10.1016/j.watres.2016.07.027

Randtke, S. J., Peltier, E. F., Adams, C. D., Lane, R. F., Breault, Z. A., Carter, R. E., & Roberson, J. A. (2017). *Evaluation of Water Service Line Lining and Coating Technologies [Project #4351]*. Denver, CO USA: Water Research Foundation.

Ratna, D. (2009). *Handbook of thermoset resins*. Shrewsbury: Shrewsbury : Smithers Rapra Technology, Ltd.

Rigal, S., & Danjou, J. (1999). Tastes and odors in drinking water distribution systems related to the use of synthetic materials. *Water Science and Technology*, *40*(6), 203–208. https://doi.org/10.1016/S0273-1223(99)00558-2

Romero, J., Ventura, F., & Gomez, M. (2002). Characterization of paint samples used in drinking water reservoirs: Identification of endocrine disruptor compounds. *Journal of Chromatographic Science*, *40*(4), 191–197. https://doi.org/10.1093/chromsci/40.4.191

Rożej, A., Cydzik-Kwiatkowska, A., Kowalska, B., & Kowalski, D. (2015). Structure and microbial diversity of biofilms on different pipe materials of a model drinking water distribution systems. *World Journal of Microbiology & Biotechnology*, *31*(1), 37–47. https://doi.org/10.1007/s11274-014-1761-6

Satchwill, T. (2002). *The Impact of Pipe Coatings on Drinking Water Quality*. City of Calgary, Alberta Canada. http://www.nesc.wvu.edu/ecommerce/products/DW_Research/DWBLRE01DL.pdf

Sharma, V. K., Anquandah, G. A. K., Yngard, R. A., Kim, H., Fekete, J., Bouzek, K., … Golovko, D. (2009). Nonylphenol, octylphenol, and bisphenol-A in the aquatic environment: A review on occurrence, fate, and treatment. *Journal of Environmental Science and Health, Part A*, *44*(5), 423–442. https://doi.org/10.1080/10934520902719704

Shotyk, W.; Krachler, M. (2007). Contamination of Bottled Waters with Antimony Leaching from Polyethylene Terephthalate (PET) Increases upon Storage. *Environ. Sci. Technol.*, *41* (5), 1560–1563. https://doi.org/10.1021/es061511+

SWRCB (State Water Resources Control Board). (2014). California State Water Control Board. *Recommended Testing Procedure Following Steel Water Tank Coating Applications*. California State Water Control Board. Steel Tank Coating Requirements. July 2014. Sacramento, CA USA.

Tan, J., Jia, Z., Sheng, D., Liu, X., & Yang, Y. (2012). Effect of the molecular structure of polyurethane elastomers on the thermomechanical properties of PUE/PC blends. *Journal of Applied Polymer Science, 124*(1), 412-420. doi:10.1002/app.35114

Tan, J., Jia, Z., Sheng, D., Liu, X., & Yang, Y. (2012). Effect of the molecular structure of polyurethane elastomers on the thermomechanical properties of PUE/PC blends. *Journal of Applied Polymer Science, 124*(1), 412-420. doi:10.1002/app.35114

Turi, E. (1981). *Thermal characterization of polymeric materials*. New York: New York : Academic Press.

Turi, E. (1981). *Thermal characterization of polymeric materials*. New York: New York : Academic Press.

USN(US Naval Research Laboratory). (1997). Washington DC Control of Lead in Drinking Water, NRL/MR/6210—97-7957. July 11, 1997.

van der Kooij, D., & Veenendaal, H. R. (2001). Biomass production potential of materials in contact with drinking water: method and practical importance. *Water Science and Technology: Water Supply*, *1*(3), 39–45. https://doi.org/10.2166/ws.2001.0052

van der Wielen, P. W. J. J., & van der Kooij, D. (2010). Effect of water composition, distance and season on the adenosine triphosphate concentration in unchlorinated drinking water in the Netherlands. *Water Research*. https://doi.org/10.1016/j.watres.2010.07.016

Visakh, P. M. (2015). *Flame Retardants Polymer Blends, Composites and Nanocomposites*: Cham : Springer International Publishing : Imprint: Springer.

Wen, G., Kötzsch, S., Vital, M., Egli, T., & Ma, J. (2015). BioMig-A Method to Evaluate the Potential Release of Compounds from and the Formation of Biofilms on Polymeric Materials in Contact with Drinking Water. *Environmental Science & Technology*, *49*(19), 11659–11669. https://doi.org/10.1021/acs.est.5b02539

Whelton, A. J.; Salehi, M.; Tabor, M.; Donaldson, B.; Estaba, J. Impact of Infrastructure Coating Materials on Storm-Water Quality : Review and Experimental Study. *J. Environ. Eng.* 2013, *139* (5), 746–756. https://doi.org/10.1061/(ASCE)EE.1943-7870.0000662.

Wicks, Z. W. J.; Jones, F. N.; Pappas, S. P.; Wicks, D. A. (2007). *Organic Coatings: Science and Technology (3rd Edition)*; Hoboken, N.J. :Wiley-Interscience. https://doi.org/10.1002/047007907X

Xue, J., Wan, Y., & Kannan, K. (2016). Occurrence of bisphenols, bisphenol A diglycidyl ethers (BADGEs), and novolac glycidyl ethers (NOGEs) in indoor air from Albany, New York, USA, and its implications for inhalation exposure. *Chemosphere, 151*, 1-8. doi:https://doi.org/10.1016/j.chemosphere.2016.02.038

Zeus Industrial Products, Inc. *Performance of High Temperature Plastics*. (2005). Retrieved from Technical Whitepaper.

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