Cultivating Sustainability:

Assessing the Viability of Bio-Based Resins in Composite Manufacturing

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Assessing the Viability of Bio-Based Resins in Composite Manufacturing

by

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“The greatest threat to our planet is the belief that someone else will save it.”

- Robert Swan

Preface

This work is lovingly dedicated to my grandfather, Dimitris Apostolidis, whose memory and teachings continue to inspire and guide me. His wisdom, spirit, and enduring love have been a beacon throughout my life, and it is in his honor that I present this thesis.

The successful culmination of this research owes a great deal to the invaluable support of those around me. Firstly, I wish to extend my deepest appreciation to my research supervisor and professor Dr. B. (Baris) Kumru for his unwavering trust and guidance throughout this journey and the ones to follow. I am profoundly thankful for his mentorship, which has not only enriched my academic progress but has also played a pivotal role in my personal development through the diverse opportunities he has provided.

A special acknowledgment is due to William Dyer whose collaboration and expertise in the chemistry lab and characterization were invaluable to this project. Working alongside William on various aspects of this study has been both enlightening and instrumental in achieving our objectives.

My gratitude also extends to Roy Awater for his assistance in the physics lab, particularly with the use of complex equipment, and to Alexander Uithol and Chantal de Zeeuw, whose guidance in the laboratory during mechanical testing was indispensable. The Ph.D. students from the AMT department deserve a heartfelt thank you for their endless support, engaging discussions, and insightful suggestions, which significantly contributed to overcoming numerous challenges in this study.

This journey would not have been the same without the love and support of my friends and family. Their constant encouragement and presence during both the highs and lows of this academic endeavor have been a source of unwavering strength and motivation.

This thesis is structured to first lay the theoretical groundwork, followed by a detailed account of the experimental approach, findings, and their implications. The final chapters discuss the broader context of the study and suggest directions for future research.

As I look ahead, this research has not only solidified my commitment to sustainable engineering but has also ignited a desire to further explore this field. My aim is to contribute meaningfully to the development of environmentally friendly materials and to inspire others in this vital endeavor.

Dimitrios Apostolidis
Delft, December 2023

Abstract

Title: Cultivating Sustainability: Assessing the Viability of Bio-Based Resins in Composite Manufacturing

Research Question: To what extent it is possible to use bio-based resins for composite manufacturing?

This thesis explores the potential of sustainable resins in composite manufacturing, focusing on bio-based benzoxazine resins and bio-based epoxy derived from brown algae. The research investigates the feasibility of integrating these sustainable alternatives into composite structures. Bio-based benzoxazine resins were synthesized in-house, utilizing m-guaiacol, furfurylamine, sesamol, paraformaldehyde, Jeffamine T403, and DDS, while a commercial bio-based epoxy, phloroglucinol triepoxy (PHTE), was employed. The study involves comprehensive material analysis and testing, including an examination of chemical properties and mechanical performance. The findings reveal contrasting outcomes for the two types of bio-based resins. Bio-based benzoxazine resins exhibited challenges, as curing was not achieved, preventing their combination with composites. In contrast, phloroglucinol triepoxy, the bio-based epoxy from brown algae, emerged as a promising candidate for sustainable composite investigations. This resin demonstrated excellent mechanical properties, although its high viscosity and reactivity posed challenges for traditional manual manufacturing techniques. Furthermore, resin characterization unveiled a high glass transition temperature (Tg) system, especially noteworthy given the use of an aliphatic curing agent and monofunctional reactive diluent that lowers crosslinking density. This opens the door to its application in composites across various industries.

Key words : Bio-based resins, composite manufacturing, bio-based benzoxazine resins, phloroglucinol triepoxy, sustainable materials, mechanical properties, glass transition temperature, bio-based carbon, brittleness, environmental sustainability.

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Nomenclature

Abbreviations

Abbreviation	Definition
AEW	Amine Equivalent Weight
BADGE	Bisphenol A Diglycicyl Ether
BPA	Bisphenol A
BPF	Bisphenol F
CD	Constant Deformation
CR	Constant Rotation
CS	Constant Stress
DCM	Dichloromethane
DDS	4,4 Diamiphenyl Sulfone
DI	De-Ionized
DMTA	Dynamic Mechanical Thermal Analysis
DSC	Differential Scanning Calorimetry
DTG	Differential Thermogravimetry
EEW	Epoxy Equivalent Weight
FRPC	Fiber Reinforced Polymer Composite
FTIR	Fourrier Transform Infrared
GC	Gel Content
NIR	Near Infrared
NMR	Nuclear Magnetic Resonance
PHTE	Phloroglucinol Triepoxy
RBF	Round Bottom Flask
ROP	Ring Opening Polymerization
RT	Room Temperature
RTM	Resin Transfer Molding
SEM	Scanning Electron Microscopy
TGA	Thermogravimetric Analysis
WA	Water Absorbance
WCA	Water Contact Angle

Symbols

Symbol	Definition	Unit
E_a	Activation Energy	J mol^-1
F	Force	[N]
G’	Storage Modulus	[Pa]
G”	Loss Modulus	[Pa]
L	Length	[m]
m	mass	[kg]
R	Gas Constant at 8.3145	[J mol^{-1} K^{-1}]
T	Temperature	[K]
t	Thickness	[m]
V	Constituent Content	[-]

Symbol	Definition	Unit
m	Mass	[kg]
w	Width	[m]
β	Heating Rate	[K/min]
ϵ	Strain	[-]
η	Viscosity	[Pa· s]
ρ	Density	[kg/m^3]
σ	Stress	[Pa]
τ	Shear stress	[Pa]

1

Introduction

In recent years, there has been a growing concern within various industries regarding the environmental impact of traditional manufacturing processes and materials. The focus has primarily been on reducing carbon footprint and decreasing reliance on materials such as phenolic by-products while ensuring that product performance remains uncompromised.

One promising solution that has gathered considerable attention is the utilization of bio-based resins in composite manufacturing. Composite materials find widespread applications in key sectors like aviation, automotive, and marine industries due to their exceptional mechanical properties, durability, and lightweight characteristics. However, a significant proportion of these composites is currently produced using conventional petroleum-based epoxy resins, derived from non-renewable resources and often involving toxic precursor materials. This results in a life cycle that has adverse environmental implications.

Bio-based resins, synthesized from renewable biomass sources such as plant oils, lignin, and algae [1], offer a compelling environmentally-friendly alternative to conventional resins. Their adoption helps reduce dependence on fossil fuels, contributes to climate change mitigation, and aligns with the pursuit of a more sustainable future. Numerous industries are increasingly embracing these technologies. Beyond their environmental benefits, bio-based resins exhibit intrinsic advantages, often rivaling or surpassing those of traditional resins. They frequently demonstrate impressive tensile strength, stiffness, impact resistance, and favorable chemical properties, making them versatile for a wide range of applications [2]. Similar to conventional resins, bio-based resins can be seamlessly integrated into various composite manufacturing techniques such as wet layup, pultrusion, compression molding, and filament winding to fabricate high-quality composite structures. The comprehensive integration and utilization of bio-based resins in composite structures and manufacturing pose several challenges, despite their considerable merits. These challenges include cost considerations, complexities in scaling up production, and the need to identify compatible manufacturing processes [2]. Addressing these challenges necessitates sustained research and development efforts in the field of bio-based resins to unlock their full potential for sustainable composite material production.

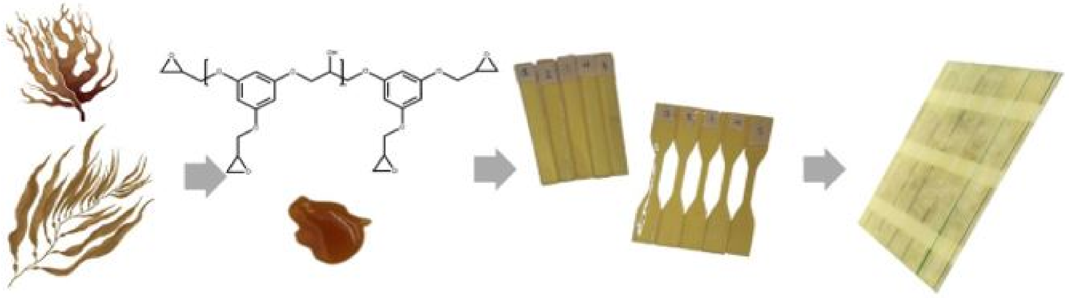
In the field of composite manufacturing, innovation through the incorporation of bio-based resins marks a pivotal milestone in the quest for sustainability. The ongoing research and development efforts in this field are not only expanding the range of available bio-based resin options but also optimizing their properties for diverse applications. As industries increasingly recognize the importance of environmental responsibility, bio-based resins are becoming a main point of material innovation. Companies and researchers are actively exploring ways to enhance the performance characteristics of bio-based resins, making them more competitive with traditional petroleum-based counterparts. This innovation is driven by a shared commitment to reducing the environmental impact of composite manufacturing while simultaneously meeting the stringent performance requirements of various industries.

The drive for sustainability in composite materials manufacturing is gaining momentum. Bio-based resins and innovative options like Benzoxazines are at the forefront of this transition toward eco-friendly materials. Nevertheless, challenges persist and necessitate ongoing research and development endeavors to fully harness the potential of these materials, thereby fostering a more sustainable future for various industries.

In the context of resin innovation, the significance of bio-based Benzoxazines has to be explored. Benzoxazines are organic compounds with a unique ring structure. They can polymerize in a single step to form high-performance thermosetting polymers. These compounds offer not only the environmental benefits associated with bio-based resins but also specific advantages linked to their chemical properties. Benzoxazines are renowned for their toughness, high-temperature resistance, and excellent flame retardancy, making them an attractive alternative to traditional epoxy resins. Given their eco-friendly composition, distinct from typical petrochemical sources, they represent a sustainable choice for composite manufacturing. The inclusion of Benzoxazines in the array of resin options expands the toolkit for creating eco-conscious composites.

This thesis seeks to delve into the uncharted territory of sustainable resins, specifically focusing on the potential application of bio-based resins as a greener alternative in composite materials. The research places a special emphasis on two types of bio-based resins: benzoxazine resins synthesized from naturally derived precursors and epoxy resin derived from brown algae.

The development and application of bio-based benzoxazine resins, synthesized using eco-friendly raw materials such as m-guaiacol, furfurylamine, sesamol, paraformaldehyde, Jeffamine T403, and DDS, present a novel approach to creating composites with a reduced environmental impact. In parallel, the study leverages a commercially available bio-based epoxy, specifically phloroglucinol triepoxy (PHTE), to understand its suitability and performance in the context of sustainable composite fabrication.



Central to this study is a rigorous material analysis and testing regime that assesses the chemical and mechanical properties of these resins. By doing so, this thesis aims to contribute to the emerging body of knowledge on the applicability of sustainable resins in practical engineering applications. The results of such assessments are examined, comparing the performance and viability of each resin type within composite structures.

Early indications from the study suggest a dichotomy in performance. The bio-based benzoxazine resins, despite their sustainable appeal, presented significant challenges. The difficulties in achieving adequate curing hindered their potential integration with composite fibers. Conversely, phloroglucinol triepoxy resin showcased more promise. Derived from brown algae, this bio-based epoxy exhibited commendable mechanical properties but was not without its own challenges, particularly in its viscosity and reactivity, which complicate its use in traditional manual composite manufacturing methods.

In addition, this thesis discussed the thermal characteristics of the bio-based epoxy resin system, particularly its high glass transition temperature, an attribute amplified by the use of an aliphatic curing agent and a monofunctional reactive diluent aimed at reducing crosslinking density and viscosity. The implications of these findings suggest a promising but complex path forward for the use of sustainable resins in composites, with particular consideration of the requirements and constraints across different industrial applications. The following chapters will detail the experimental procedures, observations, and analyses that support these findings, thereby framing the context for sustainable resin application in the future of composite manufacturing.

2

Literature Review

In this chapter, the performed literature review before the initial stages of the research is briefly presented and discussed so that readers can familiarize themselves with the different concepts and gain some background information. In the initial phases of the literature study the focus was placed on conventional benzoxazines, their applications as well as the possibility of bio-based alternatives. Throughout the phases of the study, the literature was expanded to include conventional epoxies and their bio-based substitute. The possible material characterization techniques that could be used to obtain the chemical and mechanical properties of monomers and polymers as well as the different composite manufacturing processes currently being used are discussed.

2.1. Benzoxazines

Benzoxazine resins, also known as polybenzoxazines, have emerged as superior alternatives to phenolic-based resins, and their usage has seen a significant surge in recent years [3]. Benzoxazines refer to a group of isomeric heterocyclic compounds that consist of both a benzene ring and an oxazine ring fused together [4]. These compounds exist in eight different isomeric forms, depending on the position of the methylene group, as illustrated in Figure 2.1.

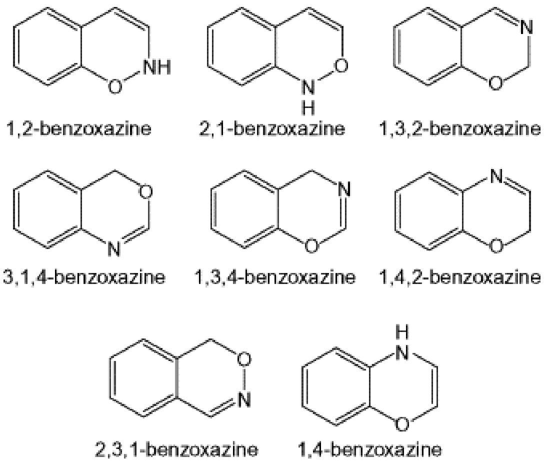


Figure 2.1: Eight Isomers of Benzoxazine [5]

2.1.1. Conventional Benzoxazines

These thermoset resins exhibit a wide array of desirable properties, including a high glass transition temperature (T_g), excellent mechanical characteristics, flame resistance, high thermal and chemical resistance, low water absorption, all while maintaining cost-effectiveness [6, 7, 8, 9]. Consequently, benzoxazines have found extensive applications in various fields, including composites, electronic circuit boards, blends, and vacuum pump rotors [3, 10, 11].

While the first synthesis of benzoxazine monomers dates back to Holly and Cope in 1944 [12],it was not until the 1990s that benzoxazines started being used as thermoset materials due to the solvent-less synthesis process that was introduced by Ning and Ishida[1] [13]. This can be attributed to some of the disadvantages of benzoxazines, especially with respect to conventional phenolic resins and epoxies. In most cases, the synthesized monomers are solid, making it difficult to process them, create films for composite manufacturing, or obtain complex structures [14]. Furthermore, the brittleness and toughness of the final benzoxazine resins impede use in multiple industrial applications [15]. It is understandable that in order for the use of benzoxazines to be increased and for them to be used in different and new fields, the toughness should be improved. Chunli et al. (2020) report different approaches that can be utilized in order to decrease the brittleness of benzoxazines, increasing their toughness; (i) introduction of various toughening agents, such as rubber, into the resin [16] (ii) design of tough benzoxazines, including soft segments (iii) introduction of nanoparticles in the final product [17].

In order to fully grasp and understand how each of the aforementioned processes works as well as obtain a better understanding of the properties of benzoxazines, one must first understand the method and process used for the synthesis of the benzoxazine monomer and consequently polymers. Usually, for the synthesis of Benzoxazines, an aldehyde, an amine, and a phenol are required [18] :

- **Phenols :** Phenols, bearing hydroxyl (-OH) groups, are essential constituents in polybenzoxazine compositions, facilitating cross-linking, a critical step in resin polymerization [14]. These compounds enhance thermal stability, mechanical strength, and chemical resistance, broadening applications [19]. They react with other phenols or amines, forming covalent bonds and a network structure, defining polymer properties. Primary phenols used include cresol, bisphenol A and F, and resorcinol [14]. Phenol choice hinges on desired properties, processing conditions, and cost. Phenol selection significantly impacts end-product properties due to varying reactivity, leading to diverse cross-linking degrees in monomer and polymer synthesis, yielding unexpected outcomes.
- **Amines :** Amines play a crucial role in benzoxazine synthesis, with their selection significantly impacting the resultant properties. Amines with varying functionalities are used. Mono-functional amines, similar to conventional epoxy curing agents, have a single amino group, promoting cross-linking by reacting with epoxy groups in benzoxazine monomers [20]. Bis-functional amines, featuring two amino groups, act as coupling agents, enhancing cross-linking by engaging with two epoxy groups. Increasing the amino groups in the amine structure, such as with tri-functional amines like JEFFAMINE® T-403 Polyetheramine, can enhance mechanical properties but may increase brittleness [21]. Amine choice with different functionalities results in polymers with varying properties: mono-functional amines for curing, bis-functional amines for increased cross-linking, and tri-functional amines for highly cross-linked networks.
- **Aldehydes :** Aldehydes are vital in polybenzoxazine synthesis, acting as curing agents to enable cross-linking among phenolic components, forming the polymer matrix [22]. Formaldehyde and paraformaldehyde are commonly used aldehydes in this process. The amount and chemical structure of the aldehyde integrated into polybenzoxazine synthesis significantly impact polymer properties, affecting rigidity and thermal stability [23]. Excessive aldehyde content can lead to increased brittleness and reduced ductility in benzoxazine polymers.

The benzoxazine monomers can be obtained through a Mannich-like condensation process [24]. Given the abundance of both commercial amines and phenolics, various different benzoxazine monomers can be synthesized so that various specific applications and fields can be covered [14]. However, it has been determined and reported that even though monofunctional benzoxazine monomers can form a linear polymer, the final obtained polymer does not have a large molecular weight (Reiss et al., 1985). This is the result of the chain growth being terminated at the dimer length as hydrogen bonds are formed at the front of the growth.

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[1] H. Ishida, United State Patent 5543516, 1996

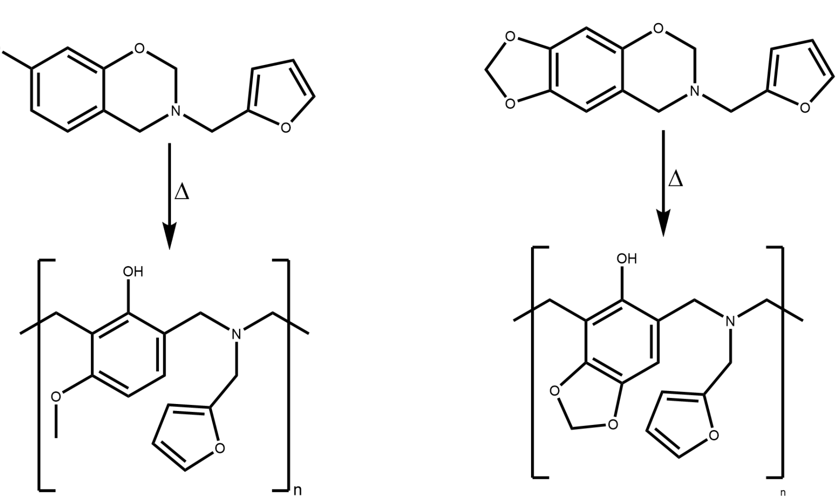


Figure 2.2: Example of Ring-Opening Polymerization of Benzoxazine Monomer

Many bis-functional benzoxazines are used to obtain crosslinked polymers with useful properties. While molecular connectivity has been improved, interference with chain growth by hydrogen bond formation has not changed.

The polymerization of benzoxazines is highly dependent on temperature and upon certain conditions, due to the six-member ring strain (oxazine ring) in the benzoxazine structure [25][19]. Benzoxazines undergo **R**ing-**O**pening **P**olymerization (**ROP**) at elevated temperatures, typically in the range of 100-200°C. Ring-opening polymerization is a polymerization process in which cyclic monomers are opened and reacted with themselves or with other monomers to form a linear polymer chain. This reaction can occur through a variety of mechanisms, depending on the structure and reactivity of the monomer and the reaction conditions. At these temperatures, the benzoxazine monomer is converted into a highly reactive activated intermediate that can undergo ROP with itself or other monomers, resulting in the formation of a polymer chain. A more detailed explanation of the ROP mechanism regarding benzoxazines is given in Appendix B

The reaction rate of the polymerization increases with temperature, due to the increased thermal energy available to overcome the activation energy barrier associated with the formation of the activated intermediate. However, the reaction must be carefully controlled to prevent premature gelation or degradation of the polymer [19].

The polymerization temperature also affects the properties of the resulting polybenzoxazine. Higher temperatures generally result in polymers with higher molecular weight, improved thermal stability, and better mechanical properties. However, excessively high temperatures can lead to thermal degradation of the polymer and the formation of unwanted byproducts.

Overall, the polymerization of benzoxazines is a highly temperature-sensitive process, and careful control of the reaction conditions is required to achieve optimal polymerization and to obtain polymers with desired properties. In benzoxazines, ROP occurs when the oxazine ring is opened by the addition of a nucleophile, such as a catalyst or another benzoxazine monomer. The activated intermediate formed by the opening of the oxazine ring then undergoes further nucleophilic attack, resulting in the formation of a covalent bond and the extension of the polymer chain. This process is repeated until all of the monomers are consumed or until the reaction is terminated by the addition of a chain terminator.

2.1.2. Bio-based Benoxazines

Traditional benzoxazines rely on petroleum-derived materials and are not environmentally friendly. In recent years, the development of bio-based benzoxazines has gained significant attention due to their potential as sustainable alternatives to petroleum-based materials. Recent advancements in the synthesis and characterization of bio-based benzoxazines are discussed, compared to traditional benzoxazines and epoxies, and their applications are explored in composites.

Using bio-renewable resources such as lignin, tannins, and plant-based oils, bio-based benzoxazine resin systems can be synthesized [26]. The resulting polymers exhibit improved environmental performance, reduced carbon footprint, and decreased dependency on petroleum-based resources. Several examples and studies on the synthesis of benzoxazine resins from natural precursors are available [27]. For instance, Minighera et al. [28] synthesized a bio-based benzoxazine based on cardanol, a phenol obtainable from processing cashew nut shell liquid. This product exhibited good thermal stability, high char yield, and strong mechanical properties [28]. Similarly, extensive research on bio-based benzoxazines derived from lignin and its byproducts has been conducted. It has been observed that lignin-based benzoxazines are excellent flame retardants, due to the presence of phenolic hydroxyl groups in their chemical structure [29].

Caifei et al. [4] synthesized fully bio-based benzoxazine monomers, 3-furfuryl-8-methoxy-3,4-dihydro-2H-1,3-benzoxazine (Bzf) and 3-octadecyl-8-methoxy-3,4-dihydro-2H-1,3-benzoxazine (Bzs), via a solventless method based on furfurylamine, paraformaldehyde, and guaiacol, and on stearylamine, paraformaldehyde, and guaiacol. Their structures, as shown in Figure 2.3, have been confirmed through various characterization techniques, including FTIR spectroscopy, NMR spectroscopy, and elemental analysis.

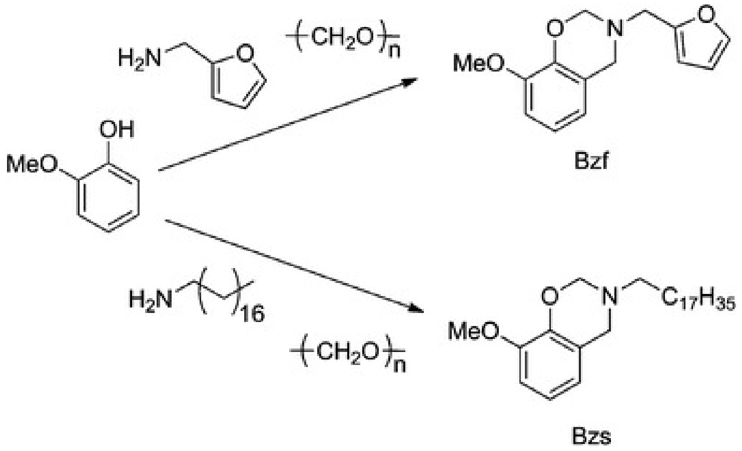


Figure 2.3: Syntheses of Bzf and Bzs [4]

When compared to traditional benzoxazines and epoxies, several advantages are evident for bio-based benzoxazines [30]. Due to the reduced use or even absence of hazardous chemicals during their synthesis, bio-based benzoxazines are less toxic. Simultaneously, their renewable nature and reduced carbon footprint contribute to better environmental performance. The presence of phenolic groups in the polymer structure results in improved mechanical properties compared to conventional epoxy systems [31]. These phenolic groups lead to enhanced crosslinking and high char yield during thermal degradation. A recent study compared the mechanical properties of a bio-based benzoxazine derived from thymol with those of a traditional benzoxazine [32]. The bio-based product exhibited higher tensile strength and modulus, suggesting its potential use in high-performance applications.

Bio-based benzoxazines have the potential for use in composites due to their excellent mechanical properties and thermal stability. Several studies have reported the incorporation of bio-based benzoxazines into various matrices, including epoxy, phenolic, and polyurethane [30]. These composites exhibited similar mechanical properties and thermal stability compared to pure epoxy. Similarly, Liu et al. synthesized a bio-based benzoxazine from rosin to be incorporated into a phenolic resin [33]. However, in-depth investigations into composite structures have not been extensively explored.

The development of bio-based benzoxazines has gained significant attention due to their potential as sustainable alternatives to petroleum-based materials. Their excellent mechanical properties and thermal stability make them promising candidates for composites. Further research is needed at various stages of the bio-based benzoxazine utilization process, from synthesis and characterization to their application in composite manufacturing. It is evident that exploring the use of bio-based benzoxazine resin for composite manufacturing would be highly beneficial. Below, some studies and pre-cursors used in the synthesis of bio-based benzoxazines are discussed:

Guaiacol and M-guaiacol are phenolic compounds with similar chemical structures, both important in the synthesis of polybenzoxazines. They serve as curing agents, facilitating cross-linking among phenolic constituents to form the polymer matrix [22]. Guaiacol, known as 2-methoxyphenol, has a benzene ring with a methoxy ($-OCH_3$) group attached to the second carbon atom of the ring. M-guaiacol, or 3-methoxyphenol, is structurally similar but with the methoxy group attached to the third carbon atom of the benzene ring. Both compounds share the chemical formula $C_7H_8O_2$. The primary difference is the position of the methoxy group on the benzene ring, potentially affecting precursor properties and reactivity. The production of bio-based M-guaiacol can involve biomass or plant-derived materials, depending on factors like cost and purity requirements. Natural sources, like the guaiacum tree and wood smoke, can yield M-guaiacol [34]. Synthetic production from catechol is another option [34].

Sesamol, derived from sesame seeds and sesame oil, is a natural compound gaining attention in various industries due to its antioxidant properties [35]. In polymer science, it’s been used to develop benzoxazine monomers, offering potential applications in coatings and more [36].

Furfurylamine, a bio-derived compound, has been explored for bio-based benzoxazine synthesis. It can be produced from biomass or agricultural waste products through processes like furfural reduction [37]. Similarly, Jeffamine polyetheramines have been used to synthesize benzoxazine resins, impacting monomer properties and applications [38][39].

Paraformaldehyde, with the formula (CH_2O)n, is a crucial component in benzoxazine synthesis, acting as a curing agent to crosslink phenolic compounds [4][40][38]. Its use is integral to benzoxazine formation, including bio-based benzoxazine resins.

2.2. Epoxies

Epoxy resins are a widely used class of synthetic polymers known for their exceptional bonding properties and durability. These materials are derived from a combination of epoxy monomers and hardening agents, which, when mixed together, create a strong and resilient adhesive or coating. Epoxy resins are renowned for their ability to bond various materials, such as metals, plastics, wood, and concrete, providing a strong and long-lasting connection. They are commonly employed in a wide range of applications, including construction, automotive, aerospace, electronics, and art, owing to their remarkable strength, chemical resistance, and versatility. The versatility of epoxies, both as adhesives and coatings, has made them an indispensable component in numerous industries.

2.2.1. Conventional Epoxies

Polymer composites use polymer matrices and various fillers across different lengthscales (nano to macro) to construct advanced materials with upgraded functions; i.e. conductivity, photoactivity, and mechanical reinforcement. **F**ibre-**R**einforced **P**olymer **C**omposites (**FRPC**) shaped modern aviation, automotive and wind turbine industries by presenting lightweight, durable, and mechanically superior structures. Thermosetting resins are the dominant class of matrices used for reinforcing fibers, such as carbon and glass, using manufacturing engineering to form defect-free structures. Currently, the composite market is dominated by the use of **Dig**lycidyl **E**ther of **B**isphenol **A** (**DGEBA**) as epoxy monomer, which is generated through the reaction of Bisphenol A with epichlorohydrin in presence of base. Hardener is selected among multifunctional amines or anhydrides based on the target application and provides an exothermic ring-opening reaction with multifunctional epoxy monomers to form a thermoset. Additives such as reactive diluents and accelerators are found in delicate industrial resin recipes to adjust processability and curing cycles.

The synthesis of traditional epoxies involves the chemical reaction between epoxy resins, often derived from compounds like **B**isphenol-**A** (**BPA**) or **B**isphenol-**F** (**BPF**), and curing agents that may include amines, anhydrides, or acid catalysts. This reaction process leads to the creation of a crosslinked polymer network, achieved through the ring-opening polymerization of epoxy groups [41].

Traditional epoxies boast a broad spectrum of applications across various industries, primarily owing to their versatility. In the aerospace sector, they play a pivotal role in the production of composite materials and the bonding of structural components due to their remarkable strength-to-weight ratio [41]. In the electronics industry, they find utility as encapsulants and adhesives for semiconductors and electronic devices [42]. In the automotive domain, epoxies are embraced for their impact resistance and corrosion protection [43]. Furthermore, epoxies feature prominently in marine applications, construction projects, and numerous other fields.

The properties of traditional epoxies are subject to a multitude of influencing factors. The resin-curing agent ratio, curing conditions, and specific formulation can yield resins with distinct properties, offering both advantages and disadvantages. Traditional epoxies are distinguished by their high mechanical strength, exceptional adhesion to various substrates, and robust chemical resistance [44]. Moreover, the glass transition temperature (Tg) can be tailored by adjusting curing parameters, allowing for applications across a wide temperature range [45].

While traditional epoxies bring forth numerous advantages, including their impressive mechanical strength, outstanding adhesion, and durability, they are not without drawbacks and limitations. Environmental concerns surround their usage due to the presence of bisphenol compounds, with potential health risks associated with these compounds. Additionally, their relatively high viscosity and susceptibility to brittleness in specific formulations can restrict their application in certain scenarios [46].

In light of these environmental concerns, research efforts are directed toward finding more ecologically friendly alternatives. Bio-based epoxy formulations and sustainable curing agents are being explored as viable options, aiming to mitigate the environmental impact associated with the manufacturing and disposal of epoxy-based products [47].

2.2.2. Bio-Based Epoxies

It is important to mention that Bisphenol A (BPA) is a substance of concern as it possesses major toxicity as an endocrine disruptor. Additionally, its synthesis from fossil feedstocks (phenol and acetone in the presence of a strong acid catalyst) fails to satisfy the green chemistry principle of ‘utilization of renewable feedstocks’. Hence, polyphenolic compounds from renewable resources spark interest to replace BPA and other petroleum-derived chemicals for epoxy resin formations.

Numerous studies have explored the potential of bio-based epoxies as sustainable alternatives to petroleum-based epoxy resins, with a focus on formulations derived from renewable resources.

One area of investigation involves soybean oil-derived epoxy resins, aiming to replace petroleum-based counterparts [48][49]. Researchers have optimized curing processes and found that soybean oil-based epoxy exhibits comparable mechanical properties, including tensile strength and impact resistance, to traditional epoxy resins.

Despite the utilization of renewable compounds such as citric acid, cardanol and linseed oil to form epoxy resin even on commercial scale, their aliphatic structures fail to satisfy when thermomechanical performance criteria are vital. Meanwhile, many renewable starting compounds such as resveratrol are studied for epoxy resin formation. However, the majority of research utilizes petroleum-derived analogs of such molecules while implying the potential of a generation of such molecules from renewable resources, which in reality is strictly hindered by scalability. Additionally, many articles report successful resin formation starting from renewable epoxy compounds, however, their translation into fiber-reinforced composite manufacturing is rarely defined in the literature.

Lignin, a byproduct of the paper and biofuel industries, has also been studied as a raw material for bio-based epoxy resins [50]. Incorporating lignin-derived epoxy resins into carbon fiber composites has resulted in improved interfacial adhesion and thermal stability compared to conventional epoxy matrices [51].

In contrast to benzoxazine resins, bio-based epoxies have found broader applications across industries. They are used in construction for bonding and protecting surfaces like concrete and steel structures, owing to their excellent adhesion properties and resistance to environmental degradation. Additionally, these resin systems are employed in electronics and electrical industries for encapsulation and insulation due to their low dielectric constant and good thermal stability, ideal for protecting electronic components.

Phloroglucinol is a naturally occurring aromatic compound found in specific plant and marine species, particularly in brown algae. Its origins can be traced to the isolation of phloretin, a compound initially obtained from fruit trees. Furthermore, the production of phloroglucinol can be achieved through the bioconversion of sugar derivatives [52]. This compound can be chemically modified by adding epoxy groups, resulting in the creation of **PH**loroglucinol **T**riepoxy (**PHTE**), a trifunctional epoxy monomer. PHTE is valued for its unique chemical structure and reactivity, making it suitable for various applications. Resin formulation using PHTE in the presence of anhydride hardeners has been reported by Mija et al., whereas they further pursued carbon fiber-reinforced polymer composite formation using PHTE-based resin with ester bonds exhibiting recyclability with the matrix dissolving in ethylene glycol solution at 170°C after 2.5h

2.3. Characterization Techniques

For the goal and scope of this study, the different chemical and mechanical properties of the synthesized monomers, as well as those of the commercially bought epoxy, have to be investigated and characterized. Some of the different, potential characterization techniques that are being used and could be utilized for this study are summarised and described below:

1. **Nuclear Magnetic Resonance (NMR)**:

   Hydrogen **N**uclear **M**agnetic **R**esonance spectroscopy (**HNMR**), is an analytical technique used to elucidate the structure of organic molecules by examining the magnetic properties of hydrogen atoms within the molecule [53]. In this process, the sample under investigation is first dissolved in a solvent and then exposed to a strong magnetic field, followed by radio-frequency radiation exposure [54]. As a result, the hydrogen atoms within the molecule absorb and subsequently emit this energy in the form of radio waves.

   A detector captures the emitted waves and the frequencies associated with hydrogen atoms. By measuring both the intensity and frequency of these emissions, valuable information about the neighboring atoms of the hydrogen can be gleaned. This process allows for the identification of the molecule's structure and chemical composition to a high degree of precision. The number of distinct peaks observed in the resulting spectra provides insights into the diverse chemical environments in which the atoms are situated.

2. **Differential Scanning Calorimetry (DSC)**:

   Differential **S**canning **C**alorimetry (**DSC**), primarily measures the heat flow of a sample as it undergoes heating or cooling. This technique allows for the determination of various thermal properties, including phase transitions and key transition temperatures such as T_g, melting point, and T_c (crystallization temperature), applicable to samples in different states, whether they are in solution, solid, or mixed phases [55][56]. DSC proves to be a highly valuable tool with applications spanning materials science, chemistry, pharmaceuticals, and engineering. It aids in characterizing the thermal properties of a wide range of materials, including polymers, metals, and organic compounds, thereby facilitating the selection of appropriate processes and manufacturing techniques for each material.

   The fundamental principle underlying DSC is based on the measurement of heat flow and heat transfer. The apparatus consists of two distinct cells, each housing either the sample material or a reference material. Typically, the sample is immersed in a solvent, while the reference material comprises the solvent alone[56].

Energy is applied simultaneously to both cells to ensure that the temperatures change at a uniform rate. However, due to differences between the sample and the reference, variations in the energy required to maintain equivalent temperatures occur. These energy differences correspond to the heat either absorbed or released as a consequence of endothermic or exothermic reactions occurring within the sample.

3. **Dynamic Mechanical Thermal Analysis (DMTA)**:

   Dynamic **M**echanical **T**hermal **A**nalysis (**DMTA**) stands as a widely embraced technique for assessing the viscoelastic characteristics of polymers across a range of variables such as temperature, frequency, and time. DMTA operates by applying minor oscillatory stress to a polymer specimen and subsequently tracking the corresponding strain as it relates to alterations in temperature and frequency.

   Several key parameters are frequently evaluated in DMTA, encompassing the Glass Transition Temperature (Tg), Storage Modulus (E'), Loss Modulus (E"), and Damping Factor (tanδ). Tg serves as a pivotal measurement, indicating the temperature at which a polymer undergoes a transition from a glassy, rigid state to a rubbery, more flexible state. E' and E" delineate the material's elastic and viscous responses, respectively, while tanδ quantifies the dissipation of energy during deformation.

4. **FTIR Sprectroscopy** :

   The interpretation of FTIR spectra involves the analysis of various spectral regions, encompassing the near-IR, mid-IR, and far-IR segments. The mid-IR region, specifically spanning from 4000 to 400 cm^{-1}, is the most frequently employed for FTIR analysis [57]. Moreover, the mid-IR spectrum is further subdivided into four distinct regions: the single bond region (2500-4000 cm^{-1}), the triple bond region (2000-2500 cm^{-1}), the double bond region (1500-2000 cm^{-1}), and the fingerprint region (400-1500 cm^{-1}) [57]. These regions serve as key indicators of the molecule's structural composition.

   The first three regions, specifically addressing functional groups, provide crucial evidence regarding the presence of specific functional groups within the molecular structure [58]. The analysis is facilitated by reference tables that provide absorbance ranges for different functional groups, aiding in the identification of peaks and valleys. In stark contrast, the fourth region, the fingerprint region, is a unique feature for each sample [58]. Any minor discrepancies in the molecular structure can result in variations in absorbance within this particular segment of the IR spectrum. Moreover, the number of absorption peaks across the entire IR spectrum offers insights into the complexity or simplicity of the molecule.

These selected characterization techniques play vital roles in materials science, chemistry, and various other fields, enabling researchers to gain insights into the properties and behavior of materials and samples, which is crucial for scientific research and industrial applications.

3

Scope of the Research and Research Question

In this section, the foundation for the research is given by defining its general framework, articulating the primary research question, and introducing a set of sub-questions that will guide this research project. This initial phase is crucial for understanding the scope of the study and setting the direction for the research. The central research question that stems from the initial research idea is crafted as follows:

"To what extent it is possible to use bio-based resins for composite manufacturing?"

To ensure a comprehensive and structured approach to the research, six sub-questions that complement the primary research question have been formulated:

1. **Identification of Precursors:** Which precursors can be effectively employed in the synthesis of a bio-based benzoxazine resin?
2. **Bio-content Quantification:** What level of bio-content can be achieved during the synthesis of the bio-resin?
3. **Material Properties:** What are the mechanical and chemical properties of the bio-based resin, and how do they influence its potential for composite manufacturing?
4. **Composite Manufacturing Techniques:** Which conventional composite manufacturing techniques can be adapted to combine the synthesized resin with fibers for composite manufacturing?
5. **Quality Assessment:** Which manufacturing processes offer quality products similar to those produced using epoxy-based composites, and how can we determine and compare quality?
6. **Performance Evaluation:** How do the mechanical properties of a composite with a bio-based resin matrix compare to those of a conventional epoxy-based composite, and what implications does this have for practical applications?

Given the experimental nature of the proposed research, it is imperative to adhere to the fundamental principles and key aspects of experimental research. This includes several key components, including formulating and testing specific hypotheses, data collection and analysis methods, and conducting comparative studies to assess the viability of bio-based resins for composite manufacturing.

The primary hypotheses, which will serve as the cornerstones of the research, can be summarized as follows:

- **Hypothesis 1:** It is possible to synthesize a bio-based benzoxazine resin that exhibits the required properties for composite manufacturing.
- **Hypothesis 2:** Traditional composite manufacturing techniques can be adapted and effectively applied to composites with a bio-based matrix.

- **Hypothesis 3:** The mechanical and performance characteristics of a composite with a bio-based resin matrix are comparable to those of conventional epoxy-based composites, specifically those using Bisphenol-A resin.

Throughout the research process, these hypotheses will guide the experiments, data collection, and analysis, helping to draw meaningful conclusions and insights regarding the viability of bio-based resins for composite manufacturing. The subsequent chapters of this study provide an in-depth exploration of the methodology, experimental procedures, results, and discussion in the pursuit of answering the research questions and testing the hypotheses.

4

Methodology

In this chapter, the materials used, synthesis, characterization techniques and the composite manufacturing process used are described and discussed. Firstly all the different materials and the reasons for which they were chosen are described followed by the different syntheses and chemical reactions that were performed to obtain the bio-based benzoxazine resin. All the different characterization techniques, both for obtaining the chemical as well as the mechanical properties of the resins and of the composites are also presented here. Finally, the process used for the manufacturing of a composite laminate based on glass fibers and a bio-based epoxy is described.

4.1. Pre-cursors for Benzoxazine Synthesis

Following the literature study performed, several different pre-cursors such as Guaiacol, M-Guaiacol, Sesamol, Furfurylamine, 4-4 DDS, Jeffamine Polytheramine T403, and Paraformaldehyde were considered and used for the synthesis of the bio-based benzoxazines.

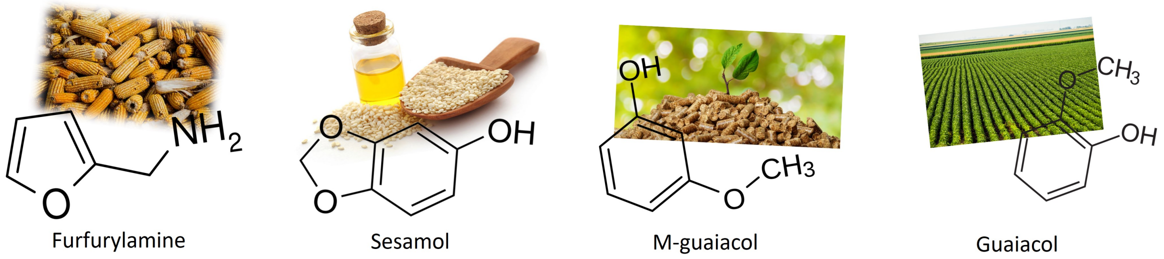


Figure 4.1: Pre-cursors used and their initial products

Guaiacol and M-guaiacol are both isomeric phenolic organic compounds. They can be produced either synthetically from catechol (benzene-1,2-diol) through methylation, or they can be naturally sourced from certain plants such as the guaiacum tree and wood smoke [34]. The research conducted by Caifei et al. [4] highlights their potential in the formation of bio-based benzoxazine resins for composite manufacturing, particularly when solventless reactions are employed.

- **Guaiacol:** Also known as 2-methoxyphenol, guaiacol consists of a benzene ring with a methoxy (-OCH3) group attached to the second carbon atom of the ring.
- **M-Guaiacol:** M-guaiacol, or 3-methoxyphenol, is structurally similar to guaiacol but features the methoxy group attached to the third carbon atom of the benzene ring.

Both compounds share the same chemical formula, $C_7H_8O_2$, but their distinct positions of the methoxy group on the benzene ring can result in differences in their properties and reactivity.

The chemical structure of guaiacol is depicted in Figure 4.2 [59].

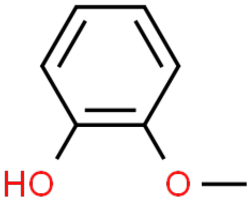


Figure 4.2: Chemical Structure of Guaiacol [59]

M-guaiacol, on the other hand, can be derived from various biomass or plant-based sources through extraction and conversion processes [60]. The choice of source and production method depends on factors like cost, purity requirements, and intended applications, making it suitable for specific niche applications or broader industrial use.

Sesamol, another bio-derived compound found in sesame seeds and sesame oil, has gained attention due to its antioxidant properties. With the chemical formula $C_7H_{10}O_3$, Sesamol is structurally related to phenol, as shown in Figure 4.3. It has found applications in the food and pharmaceutical industries and, more recently, in polymer science.

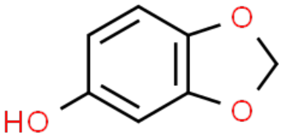


Figure 4.3: Chemical Structure of Sesamol [35]

Sesamol-based benzoxazines were synthesized by Mydeen et al. [36] for applications in hydrophobic coatings and low-k/high-k materials. Additionally, Salum et al. [40] explored the use of Sesamol in creating greener benzoxazine monomers, adhering to the Principles of Green Chemistry.

Furfurylamine, a compound with the chemical formula C_5H_7NO, has been increasingly utilized in the production of bio-based benzoxazines [36] [40]. It features a Furan ring structure with an amino group (-NH_2) attached to one of the carbon atoms in the ring, as shown in Figure 4.4. Furfurylamine can be synthesized from biomass-derived furfural, making it an attractive option for green chemistry applications.

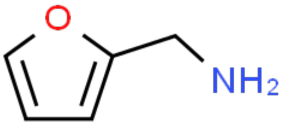


Figure 4.4: Chemical Structure Furfurylamine [61]

Jeffamine polytheramines, such as Jeffamine T-403 (depicted in Figure 4.5), have been used for creating various benzoxazine monomers. Almahdi et al. [38] investigated the role of aldehyde neighboring groups in the chemical interaction of benzoxazine precursors using different types of Jeffamine for poly-benzoxazine films. Similarly, Wan-an Cai et al. [39] utilized Jeffamine T-403 for polytheramine in the synthesis of multiple benzoxazine resins based on Bisphenol-A/Bisphenol-AF and p-formaldehyde.

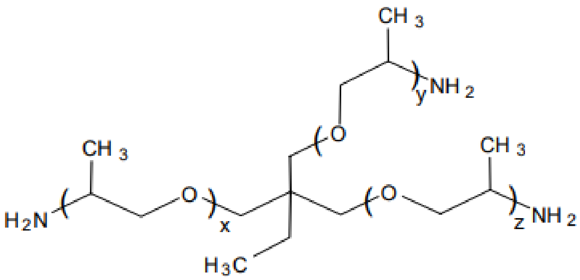


Figure 4.5: Chemical Structure of Jeffamine T403 Polytheramine

Paraformaldehyde, a vital component in the synthesis of polybenzoxazines, plays a crucial role as a curing agent for crosslinking phenolic compounds and forming polymer matrices. It features the chemical formula (CH_2O)n, where n can range from 8 to 100, and its chemical structure is shown in Figure 4.6.

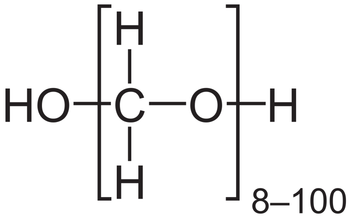


Figure 4.6: Chemical Structure of Paraformaldehyde [62]

In benzoxazine synthesis, the use of either formaldehyde or paraformaldehyde is commonplace [4] [40] [38]. This component is integral to the benzoxazine polymerization process and cannot be readily substituted with alternative precursors, even in the context of bio-based benzoxazine resins.

4.2. Bio-Based Benzoxazine Synthesis

In this section, the steps followed for the synthesis of the bio-based benzoxazine monomers are described. Initially, the synthesis method used by Cafei et al. [34] using M-guaiacol, furfurylamine, and paraformaldehyde was followed. Given the initial findings of the synthesis, a solvent had to be introduced to reduce the reactivity of the components and the exothermic behavior that was observed. Dioxane was chosen due to it being readily available in the lab and due to its use in the industry as a solvent for cellulose esters and ethers, adhesives, inks, and many other materials. In the end, six different bio-based benzoxazine monomers were synthesized using M-Guaiacol, Sesamol, and Furfurylamine; to obtain mono-functional monomers, 4,4 -Diaminodiphenyl Sulfone (**DDS**); for bis-functional monomers, Jeffamine T-403; for tri-functional monomers .

4.2.1. First Synthesis - M-Guaiacol, Fufurylamine & Paraformaldehyde

The synthesis of the first benzoxazine monomer was based on the research of Cafei et al. [34] following a simple Mannich condensation reaction. 60 g of M-Guaiacol, 47 g of Furfurylamine, and 30 g of Paraformaldehyde, so that stoichiometry balance could be achieved, were mixed together using a magnetic stirrer inside a 250 mL **R**ound **B**ottom **f**lask (**RBF**). The mixture was placed in a silicon oil bath at 100 °C, constantly being stirred, with a Graham condenser on top of it, as can be seen in Figure 4.7 to ensure that no vapors would escape as a result of increasing the temperature.

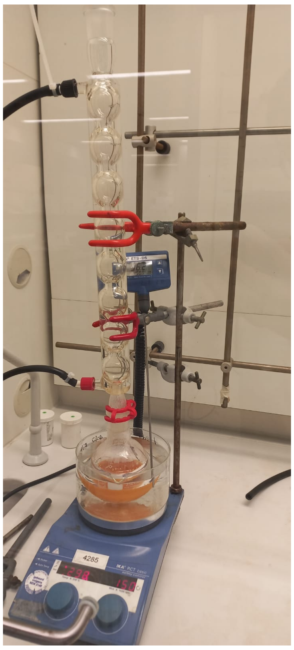


Figure 4.7: Synthesis of initial benzoxazine monomer in reflux

In contrast to the expected reaction and findings from the literature study, a violent exothermic reaction was observed once the substances were placed in the flask and started mixing them. To ensure a safe environment and that no further reactions take place due to the elevated temperature, the flask was immediately placed in an ice bath to reduce the temperature. The mixture was then placed again in the reflux system shown in Figure 4.7, where it was mixed at 100 C° for 2 hours. During mixing, precipitation was observed. The mixture was cooled down at room temperature for a full day, after which the solid sample was ground into a fine powder as seen in Figure 4.8a. The powder was placed in basic water (≈ 500 mL of 1 M NaOH) for two days so that any unreacted organic components could be dissolved and removed (Figure 4.8b). After that, the sample was washed and filtered three times with **D**e**I**onized (**DI**) water, before drying it in a vacuum oven overnight and obtaining 79 g of 3-furfury-8-methoxy-3,4dihydro-2H-1,3-benzoxazine monomer (sample named BS1).

(a) Sample ground into fine powder **(b)** Mixture in basic water **(c)** Cleaning and filtering of the monomers **(d)** Final monomer

Figure 4.8: Initial steps for synthesizing bio-based benzoxazine resin

During the initial synthesis of the first bio-based benzoxazine monomers, various stages were identified where problems could potentially arise, and unexpected outcomes were anticipated. To get started, as mentioned earlier, the initial mixing of the precursors revealed a notably energetic exothermic reaction, accompanied by the formation of preliminary crystals. This phenomenon could be ascribed to the specific placement of the methoxy group on the benzene ring of m-guaiacol. On top of that, the difficulties regarding the filtering, removing unreacted pre-cursors, and differences between the outcomes of the different syntheses showed the necessity for investigating further the synthesis steps.

4.2.2. General Synthesis Method Used

Following the initial synthesis of the bio-based benzoxazine monomer, several changes and syntheses of smaller quantities of monomers were performed to optimize the process of obtaining the benzoxazine monomers. In order to prevent the vigorous reaction observed in the initial synthesis stages, it could be advantageous to begin by combining the phenol and the amine, subsequently introducing the aldehyde. Moreover, since some of the initial precursors exist in solid form, the inclusion of a solvent could facilitate thorough and uniform mixing. Therefore, 1,4-dioxane was chosen as a solvent to dissolve the phenol and the amine fully before adding the aldehyde.

After numerous attempts and several alterations to the synthesis process aimed at obtaining bio-based benzoxazine monomers through Mannich condensation, the following synthesis steps can be summarized:

1. Add phenol and amine in a 500 mL RBF
2. Add 1,4-dioxane so that the pre-cursors could be dissolved
3. Stir for 30 minutes with a magnetic stirrer
4. Add paraformaldehyde and place the RBF in a silicon bath and in the reflux system
5. Heat the system to 100 °C and stir for 6 - 18 hours (or until precipitation is observed + 2 hours)
6. Rotary evaporate for one day to remove 1,4-dioxane
7. Dissolve monomers in **DCM** (**Dic**hloro**m**ethane) to react with unreacted amines and remove them
8. Wash mixture with basic water ($\approx 500mL$) 1 M NaOH and wash with DI water three times
9. Dry over $MgSO_4$ to remove water and filter
10. Rotary evaporate to remove DCM
11. Dry the samples overnight in a vacuum oven at 60 °C

Following the above steps and guidelines six different bio-based benzoxazine monomers were synthesized, with different pre-cursors. The chemical reactions that took place for each synthesis, as well as the exact quantities of pre-cursors used, are presented in Appendix A.

4.3. Commercial Bio-Based Epoxy

In this project, after conducting an extensive literature review, the focus was on exploring PHTE (Phloroglucinol triglycidyl) as a renewable starting material for the production of epoxy resin, through a comparison study with a BADGE system. This choice was made due to its sustainable source, trifunctional nature, and aromatic properties (as depicted in Figure 4.9), which hold the potential for delivering strong mechanical performance. It was expected that good mechanical properties would be exhibited by this monomer compared to the commercial reference sample, primarily due to the higher functionality of the monomer and the higher crosslinking density resulting from its smaller molecular weight.

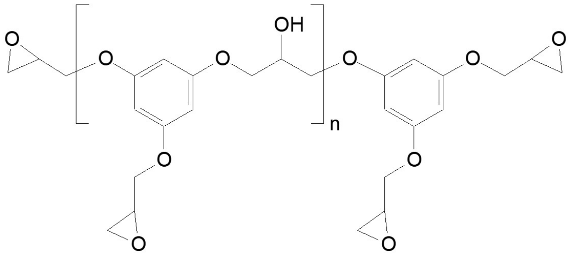


Figure 4.9: Chemical Structure of PHTE

Phloroglucinol Tris Epoxy (PHTE) with an epoxy content of 8.3 meq/g and a molecular weight of 450 g/mol was obtained from Specific Polymers and Epikure 04908 (Hexion) curing agent was chosen as a hardener. Furthermore, 1,2-Epoxy-3-phenoxypropane was chosen as a diluent to reduce the viscosity of the resin at room temperature and was purchased from Sigma Aldrich.

The resin system was generated using a mixture ratio of 2:1, based on the **E**quivalent **E**quivalent **W**eight (**EEW**) of 112 g/mol for PHTE and an **A**mino **E**quivalent **W**eight (**AEW**) of 50 g/mol for the hardener. The mixing of the resin was conducted at room temperature. The quantity of resin utilized varied depending on the specific application, taking into account the critical mixing mass. Due to the viscosity of the mixed resin at room temperature, an investigation was conducted regarding the use of a reactive diluent, 1,2-Epoxy-3-phenoxypropane, and a 10 wt.% addition of this diluent was incorporated throughout the study.

During the preparation of some resin samples for mechanical testing, the critical mixing mass was determined. 30 g of PHTE was mixed with 15 g of hardener and 4.5 g of diluent. During the degassing process, vigorous 'boiling' of the mixture was observed. This was followed by fast curing and melting of the PP bucket in which it was present, meaning that temperatures exceeding 160 °C were reached. From the above, it was determined that the critical mixing mass of the PHTE-Epikure-04908 is approximately 40 g.

Figure 4.10: PHTE-Epikure04908 mixture in Degassing Chamber

The resin and composite were thoroughly analyzed and compared to the commercial reference material, Epikote-Epikure 04098, which is based on **B**isphenol **A** **Dig**lycidyl **E**ther (**BADGE**) and features an aliphatic amine hardener.

4.4. Characterization of Monomers and Polymers

Various characterization techniques, including Fourier Transform Infrared Spectroscopy (FTIR), Thermogravimetric Analysis (TGA), Differential Scanning Calorimetry (DSC), Rheology Measurements, Density Determination, and assessments of Water Absorbance, Contact Angle, and Gel Content, have been employed to gain comprehensive insights into the properties of polymers such as benzoxazine monomers and PHTE. This chapter provides an overview of the methodologies used in characterizing these polymeric materials, with a focus on evaluating their chemical structure, thermal stability, curing behavior, rheological properties, density, and interaction with water.

4.4.1. FTIR Spectroscopy

The theory underlying Fourier Transform Spectroscopy (FT-IR) finds widespread application in scientific research and analytical reports. The spectral characteristics of substances within monomers and polymers can be assessed to determine whether the final chemical composition aligns with the anticipated outcome. This is achieved by exploiting the principle of light interference [63].In practical terms, the sample material is subjected to infrared radiation.

The FTIR spectra of both some benzoxazine monomers and of the PHTE samples were recorded using a Spectrum 100 Optica FT-IR Spectrometer, which was equipped with an attenuated-total-reflectance accessory featuring a diamond crystal. The FTIR spectra were acquired within the range of 4000 to 550 cm^{-1}, with a resolution of 1 cm^{-1}, and data were accumulated over 16 scans. For liquid samples, placement on the crystal was the procedure used for measurements. For solid samples, grinding was performed using a pestle and mortar, and these samples were securely clamped in position before measurements were initiated. Subsequently, data processing was carried out using Origin software.

4.4.2. Thermogravimetric Analysis

The investigation into the thermal stability of both the benzoxazine and the commercial epoxies was conducted through the utilization of thermogravimetric analysis (TGA). Perkin Elmer TGA 4000 Thermogravimetric Analyzer was used. To ensure precision, all measurements were executed within an inert atmosphere, specifically nitrogen (N_2), which flowed at a rate of 20 mL/min.

In the TGA experiments, samples with varying masses, ranging from 8 to 25 mg, underwent degradation across a temperature spectrum spanning from 25 to 900 °C. The heating rate applied was set at 10 °C/min. Once the temperature reached 900 °C, it was maintained for a duration of 10 minutes. The data generated by the TGA analyses were processed through Python and were visualized and interpreted using Origin software. Precise determination of the resin's thermal stability and the char yield it produced could be obtained.

4.4.3. Differential Scanning Calorimetry

In the case of the PHTE epoxy, equivalent proportions of PHTE/Epikure04098 at a 2:1 mixing ratio were prepared. The mixture was stirred for 2 minutes until it reached a homogeneous consistency and was promptly stored at -25°C to halt the curing reaction. Subsequently, DSC samples were extracted for measurement. The DSC tests were carried out over a temperature range from 25°C to 200°C, utilizing various heating rates ranging from 2.5 to 10 $°C$/min with the masses shown in Table 4.1.

Table 4.1: Settings used on DSC experiments for PHTE measurements

Heating rate (°C/min)	2.5	5	7.5	10
Sample mass (mg)	7.2	6.0	8.0	7.6

The Kissinger model was employed to calculate the activation energy of the curing reaction. The simplest form for estimating the activation energy E, using the Kissinger model is :

$$E = -R \frac{d ln \frac{\beta}{T_p^2}}{d T_p^{-1}} \tag{4.1}$$

Where:

- **R :** gas constant taken as 8.3145 $J \cdot mol^{-1} \cdot K^{-1}$
- β **:** heating rate
- T_p **:** the temperature corresponding to the position of the rate peak maximum

4.4.4. Rheology Measurements of PHTE

Rheological tests were conducted using a HAAKE MARS III rheometer. All measurements involved a mixture consisting of PHTE and Epikure 04098 in a 2:1 ratio. The following experiments were performed:

- **Viscosity at Room Temperature (RT) Over Time:** This experiment utilized the **C**onstant **S**hear (**CS**) rotational mode with a shear stress (τ) set at 1 Pa. It aimed to measure how the viscosity of the PHTE-Epikure mixture changed over time at room temperature.
- **PHTE Viscosity Across Temperature Range:** This experiment was carried out in **C**onstant **R**otation (**CR**) rotational mode with a rotational frequency of 1 Hz. It focused on examining how the viscosity of the PHTE component varied over a range of temperatures.
- **Curing Behavior of PHTE-Epikure Mixture:** This experiment involved the **C**onstant **D**eformation (**CD**) oscillation mode with a deformation (γ) of 5% and a frequency of 1 Hz. The main objective was to investigate the curing process and behavior of the PHTE-Epikure mixture during this process.

The main aim of these tests was to obtain valuable insights into the material properties and behavior of the PHTE-Epikure system under various conditions and settings.

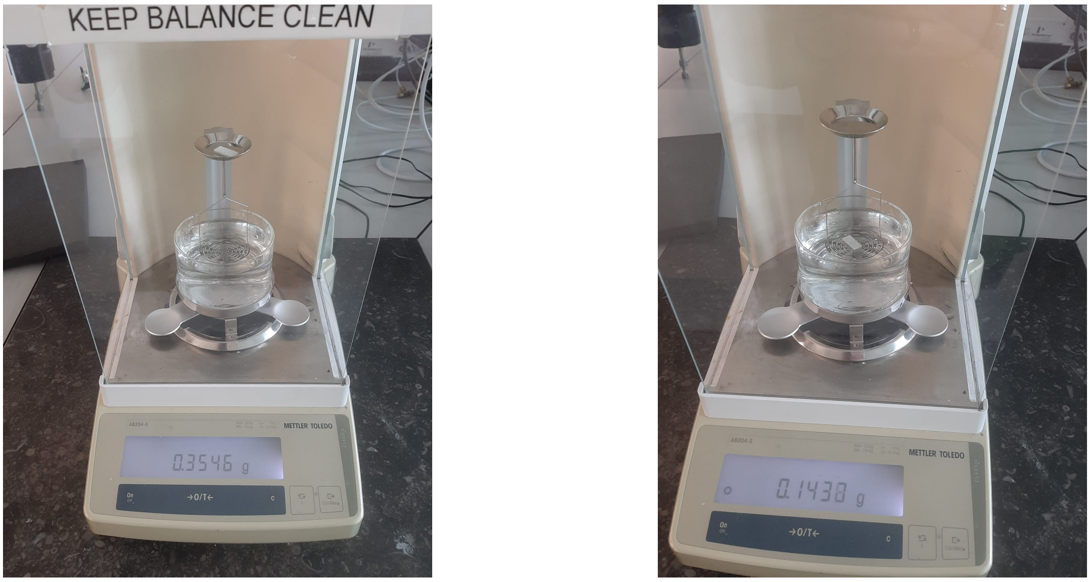
4.4.5. Density Determination

The density of cured components was ascertained in adherence to the procedures outlined in ”Standard Test Methods for Density and Specific Gravity (Relative Density) of Plastics by Displacement,” as prescribed in ASTM-D792. This involved conducting measurements on multiple individual samples and subsequently computing the average density using Archimedes' principle with the following formula:

$$\rho = \frac{A}{A-B}(\rho_0 - \rho_L) + \rho_L \tag{4.2}$$

Where:

- **A :** dry mass, which signifies the mass of the sample when measured in the air.
- **B :** wet mass, which corresponds to the mass of the sample when submerged in water.
- ρ **:** density of the sample in question.
- ρ_0 **:** density of the auxiliary liquid, and this value depends on the temperature of the liquid.
- ρ_L **:** density of air, typically considered as 0.0012 g/cm³.



(a) Determination of Dry mass A

(b) Determination of Wet Mass B

Figure 4.11: Density Determination based on Archimedes principle

Samples were prepared in accordance with the guidelines given in the standard. It was ensured that each sample should be clean and free from any surface contaminants or moisture. Once the samples were prepared and optically tested for any discrepancies, their dry mass (mass of the sample when measured in the air) was measured. The sample was then submerged in the auxiliary liquid, which in this case was DI water, and was weighed again to determine its wet mass. The different steps followed for the determination of the mass can be seen in Figure 4.11 By utilizing Equation 4.2 the density of each sample could be determined. By averaging the calculating densities, the density of the benzoxazine polymer and of the PHTE/Epikure04098 were determined.

4.4.6. Water Absorbance, Water Contact Angle and Gel Content

The water affinity of both the resin and composite based on PHTE was investigated through swelling and water contact angle tests.

The 'Water absorption of plastics' standard test as per ASTM-D5706 was utilized. Samples of both the resin and composite, with varying masses ranging from 0.3 to 0.5 g (referred to as W_0), were immersed in vials of DI water and were left for 24 hours, 48 hours, 7 days (168 hours), and 14 days (336 hours) respectively, as shown in Figure 4.12a. Subsequently, the samples were removed from the water, were wiped with filter paper, were dried with compressed air, and their weights (W_D) were recorded. The extent of water absorption was then calculated using the following formula:

$$WA\% = \frac{W_D - W_0}{W_0} * 100 \tag{4.3}$$

Where :

- W_D **:** Weight after submerging in distilled water
- W_0 **:** The initial weight of the sample

The determination of the gel content for the PHTE resin and composite was performed according to the ASTM D27655 standard, titled 'Standard Test Methods for Determination of Gel Content and Swell Ratio of Crosslinked Ethylene Plastics.' In this procedure, samples of the resin and composite were immersed in toluene for a duration of 72 hours (see Figure 4.12b). After the immersion period, the samples were removed, dried using filter paper and compressed air, and then weighed. The gel content was calculated using Equation 4.4.

$$GC\% = \frac{W_f}{W_0} \cdot 100 \tag{4.4}$$

Where:

- W_f : Mass of the dried samples after immersion in toluene
- W_0 : Initial mass of the sample before immersion

(a) Resin and Composite samples submerged in DI water

(b) Resin and Composite samples submerged in Toluene

Figure 4.12: Water absorbance and Gel Content Tests

For water contact angle measurements, the Attension Theta Optical Tensiometer, provided by KSV Instruments, was employed. A total of five resin and five composite samples, each possessing flat surfaces, were chosen for this analysis. A water droplet was carefully deposited onto the surface of each sample, and a digital image was then captured. Subsequently, the captured image underwent analysis using the Attension Theta software, which allowed for the measurement of both the left and right contact angles of the droplet in contact with the sample structure. From these measurements, the average contact angle was calculated for each sample.

4.5. Mechanical Properties of Resin

This section presents the experimental methodologies used to evaluate a novel bio-based resin system. Dynamic Mechanical Analysis was conducted on both the pristine resin and its composite form, utilizing a TA Instruments RSA-G2 DMA under single cantilever bending geometry. Precise experimental conditions, sample preparation, and the specific dimensions of the tested specimens are thoroughly described, providing a transparent overview of the testing regimen. Following this, the focus is shifted to the mechanical properties, outlining sample fabrication and the execution of tests in line with ISO 1781 and ASTM D638 standards.

4.5.1. DMA

DMA measurements were conducted using a TA Instruments RSA-G2 DMA, employing the single cantilever bending geometry. The study encompassed both the analysis of the pristine resin and the composite, which had been cured at room temperature for 24 hours and subsequently subjected to a 1-hour post-cure at 140°C. Oscillatory experiments were carried out across a temperature range of 25-180°C, employing a heating rate of 3°C/min, maintaining a constant displacement of 7.5 µm, and operating at a frequency of 1 Hz.

The specimens employed for this test were crafted from a resin mixture comprising a 2:1 ratio of PHTE to Epikure, enriched with a 10 wt.% reactive diluent with dimensions 46.26 x 9.98 x 3.41 mm. These specimens were meticulously prepared by cutting them to size with a diamond cutter, followed by precision sanding to ensure flat, uniform edges. Subsequently, they were subjected to a final post-cure at 140°C for 1 hour in an oven.

4.5.2. Flexural and Tensile Testing

The mechanical properties of the resin were examined through mechanical testing, encompassing both flexural and tensile testing. The fabrication of samples and the testing process adhered to the guidelines outlined in "Plastics-Determination of Flexural Properties" (ISO 1781) and "Standard Test Method for Tensile Properties of Plastics" (ASTM D638). For each test, five individual samples were generated following the dimensions stipulated in the standards.

Figure 4.13: PHTE/Epikure04908 flexural specimen

Figure 4.13: PHTE/Epikure04908 tensile specimen

A mixture of PHTE and Epikure0498 was combined in a 2:1 ratio, with the addition of 10wt.% of a reactive diluent. The mixture was degassed for 20 minutes to eliminate any volatile elements and ensure that no voids would be present in the specimens. Following this, they were poured into silicon molds with the required shapes, which were manufactured following the dimension guidelines provided in the standards. The exact dimensions of the specimens can be seen in Table 4.2 and 4.3.

Table 4.2: Dimensions and Remarks of the Specimen used for Flexural testing of PHTE

Sample	L (mm)	w (mm)	t (mm)	W (g)	Remarks
FR1	79.82	10.04	4.12	3.7904	Bubbles present on the edges, on the surface, at the middle of the specimen
FR2	79.72	9.90	4.18	3.6736	No obvious remarks worth mentioning
FR3	80.09	10.09	4.23	4.0680	Sample significantly thicker than the expected
FR4	79.91	9.86	3.86	3.4940	Concave shape on one side of the sample. Optical observation verified by thickness and mass measurements
FR5	79.95	9.84	4.08	3.2811	A small piece is stuck in the middle of the specimen. Potentially small part of the silicon mold

Table 4.3: Dimensions and Remarks of the Specimen used for Tensile testing of PHTE

Sample	L (mm)	w1 (mm)	w (mm)	t (mm)	W (mg)	Remarks
TR1	129.28	6.19	18.89	4.04	8.3835	Two small notches are present in the neck of the sample
TR2	129.63	6.11	18.91	3.95	8.3263	Significant amount of voids
TR3	129.33	6.19	18.99	3.94	7.9279	Good quality sample
TR4	130.2	6.13	18.80	4.03	7.6283	Significant amount of voids at the grip locations
TR5	129.27	6.09	18.88	3.93	8.0632	Good quality sample

For both tests, the Zwick and Roell 20 kN tensile machine was utilized. In the case of tensile testing, a 20 kN head was affixed as the anticipated load exceeded 1 kN. The testing speed was established at 1 mm/min, and an extensometer was positioned within the gage of the dog-bone structure. The tensile modulus was determined through the extensometer data at 0.05% and 0.25% strain. To safeguard the extensometer from damage during specimen fracture, it was disengaged from the sample once 60% of the projected maximum force was attained. In the context of flexural testing, the 1 kN load cell was mounted on the machine, and the sample was situated on the three-point-bending fixture with loading edge and support radii set at 5 mm. To ascertain the machine's precision, a compliance test involving a steel specimen was conducted. The speed of the machine's head was adjusted to 1 mm/min.

4.6. Composite Manufacturing

In this section, the preparation and manufacturing of glass fiber-reinforced composite specimens using a wet hand layup process is described. The process details the precise formulation of the PHTE/Epikure04908 resin system and the steps taken to mitigate its high reactivity, followed by the layup, curing, and post-curing procedures to produce tensile and flexural samples for mechanical testing. The section also presents visual documentation of the sample preparation stages.

During the preparation of specific pure resin samples, numerous trials, to determine the most suitable manufacturing process, primarily focusing on the hand-layup technique, were conducted. The option of vacuum infusion was considered, for its potential to yield higher-quality products with reduced volatiles and improved impregnation, however, it was ruled out due to the high cost of the PHTE monomer, amounting to approximately 600 €/100 g .

Findings from the characterization of PHTE suggested that high-speed **R**esin **T**ransfer **M**olding (**RTM**) might be a more suitable process because of the resin's high viscosity. However, for the purposes of this study, the hand lay-up method was chosen as the preferred approach for fabricating structures to evaluate the feasibility of combining the mentioned resin with reinforcement materials. Nevertheless, this choice required several small-scale tests and adjustments to determine the optimal settings and procedures. For the subsequent tests, the PHTE/Epikure04908 system was employed at a mixing ratio of 2:1. It was assumed that twice the amount of resin relative to the weight of the reinforcements, corresponding to 303 g/m^2, would be necessary for thorough impregnation. Below, different trials performed are described:

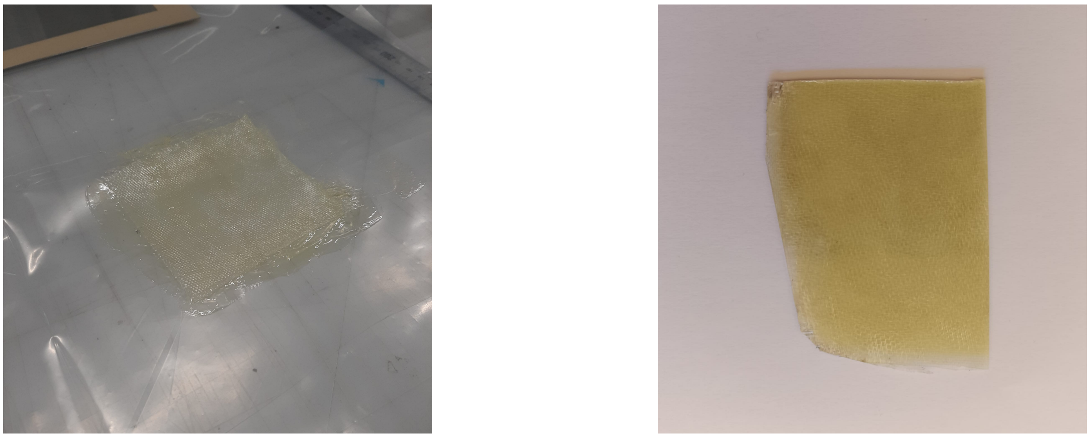
1. **Reinforcement Impregnation :** Two separate ways were considered to be used for the impregnation of the reinforcement layers with the monomer :
    - *Impregnation of the layers all at the same time :* In this approach, a small laminate consisting of four layers with a random orientation and layup was produced. The layers were stacked on top of one another, and an adequate amount of resin was poured onto the layup. Subsequently, a card or roller was used to spread the resin evenly, with the goal of achieving complete impregnation of the reinforcement material as shown in Figure 4.14a. In Figure 4.14b the laminate obtained using this method can be seen. A significant amount of dry spots and areas of fibers that have not been impregnated are observed.

(a) Applying the resin in a single application

(b) Cured laminate following 1st method

Figure 4.14: Small laminate of 4 layers made using the 1st method

- *Impregnation of each layer individually :* In this method, a small laminate composed of four layers with a random orientation and layup was created. After placing each layer, the resin was poured and spread using a card or roller, similarly to what is shown in Figure 4.15a.This process was repeated for each layer, ensuring proper impregnation before adding the next layer, until the desired layup was achieved.The resulting laminate can be observed in Figure 4.15b after it was cut to facilitate internal inspection. A simple visual inspection indicates that this process resulted in a higher-quality product.



(a) Fully impregnated laminate

(b) Cured laminate following the 2nd method

Figure 4.15: Small laminate of 4 layers made using the 1st method

In both of these processes, the viscosity of the resin proved to be problematic. In the first method, dry spots were observed on the laminate. The second method yielded a higher-quality product, but the impregnation process itself posed challenges. Therefore, it became necessary to find a way to reduce the viscosity of the resin, as was indicated by the rheological analysis findings as well.

2. **Lowering the viscosity of the system using heat :** To reduce the viscosity of the PHTE/Epikure04908 system, one approach was to maintain the mixture in a silicon heat bath at 50/60°C. After mixing PHTE/Epikure04908 at a 2:1 ratio and completing the degassing process, the mixture was placed in the heat bath. In the initial 5 minutes, there was a noticeable reduction in viscosity, making it considerably easier to impregnate the first two layers. However, approximately ten minutes into the process, a vigorous reaction occurred in the container, followed by rapid curing of the mixture, resulting in significant material waste as can be seen in Figure 4.16. These findings were corroborated by the rheological analysis conducted.

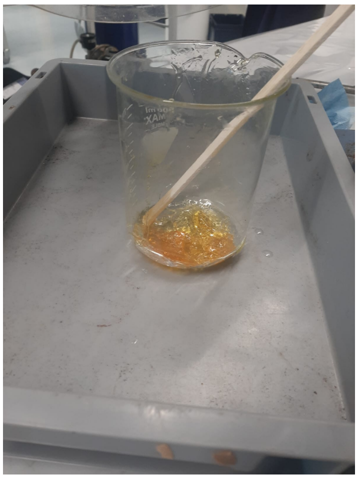


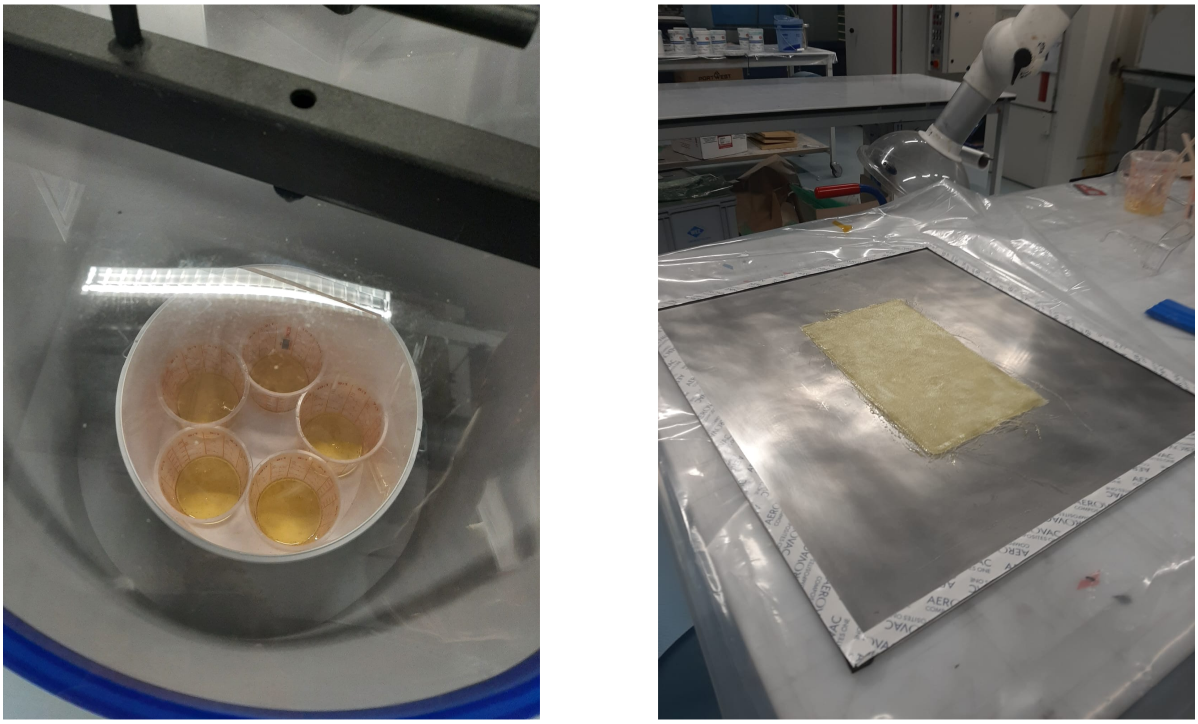
Figure 4.16: Cured PHTE/Epikure04908 system as a result of the silicon heat bath

3. **Lowering the viscosity of the system using diluent :** As was mentioned previously, due to the high viscosity of the mixed resin at room temperature, an investigation was carried out to explore the use of a reactive diluent, specifically 1,2-Epoxy-3-phenoxypropane. The amount of required diluent was investigated by incorporating 1,2,5,10 and 15 % and visually inspecting its flow and how easy it was to spread it on the layers. As a result, a 10 wt.% addition of this diluent was introduced and maintained throughout the study.

Following the aforementioned findings, a laminate could be manufactured by implementing the knowledge gained. The composite was manufactured using a wet hand layup process, utilizing HEXFORCE 7581 glass fiber satin weave with a [0,90,0,90]s layup pattern. A laminate measuring 300x160 mm was created, from which five tensile samples, each 250 mm in length and 25 mm in width, were extracted.

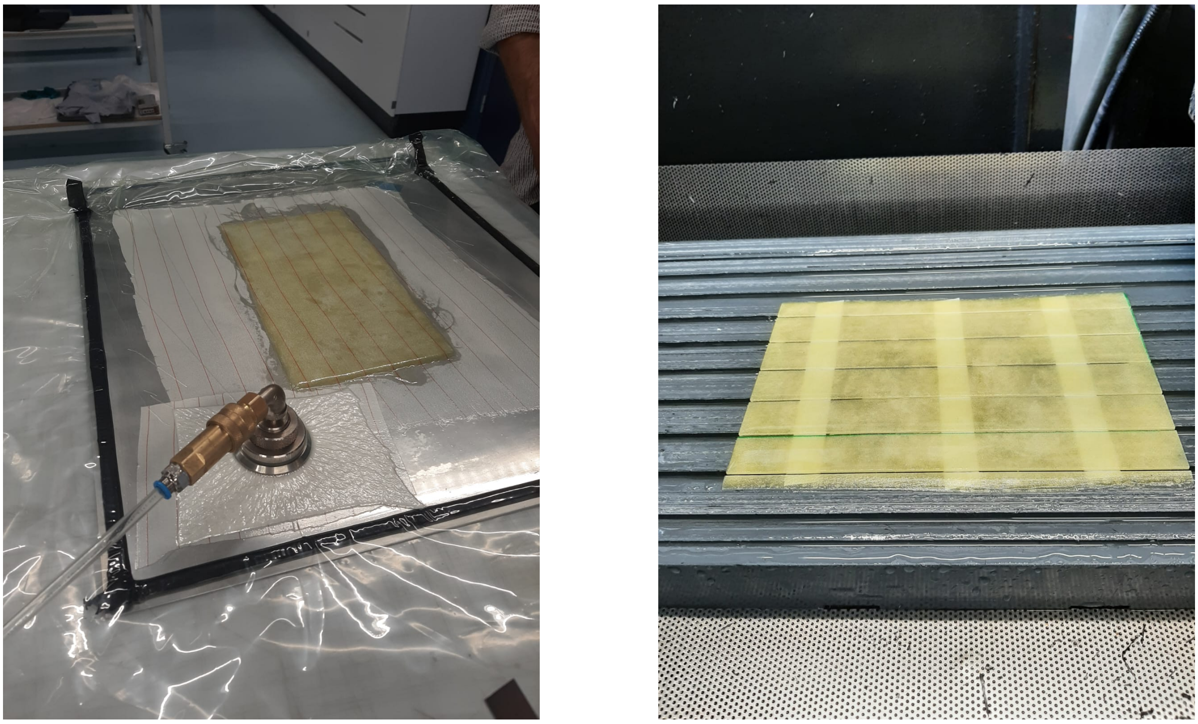
To prepare the resin, five containers were used, each containing 20 g of PHTE, 10 g of Epikure0498, and 3.3 g of 1,2-Epoxy-3-phenoxypropane as can be seen in Figure 4.17a. This was done to ensure that the critical mass of 40 g was not reached. The resin mixtures were subjected to a 20-minute degassing process to eliminate any trapped gases. During the degassing process, curing was observed in three out of the five buckets. This finding further supports the high reactivity of the PHTE-Epikure system.

Upon completion of the degassing process, each layer of the composite was thoroughly saturated with the resin by placing each layer in between two thin plastic films and spreading the resin using a card. Adequate pressure was applied to ensure thorough impregnation while ensuring that the fibers remained undistorted. Once all the layers were saturated with resin, the laminate was transferred onto an aluminum plate (as shown in Figure 4.17b), which had been coated with three layers of marble finish. placed in a vacuum bag (Figure 4.17c), and allowed to cure at room temperature for 24 hours. Subsequently, a post-curing step was conducted at 140°C for a duration of 4 hours. For a visual representation of the steps during the manufacturing process refer to Figure 4.17.



(a) Preperation of resin for Hand layup

(b) Impregnated laminate



(c) Vacuum bag and application of pressure **(d)** Final Laminate

Figure 4.17: Different steps during the manufacturing process

Similarly, a laminate was fabricated using Epikote/Epikure04908 resin, incorporating a 10% diluent. This was done to facilitate a meaningful comparison between the two distinct resin systems.

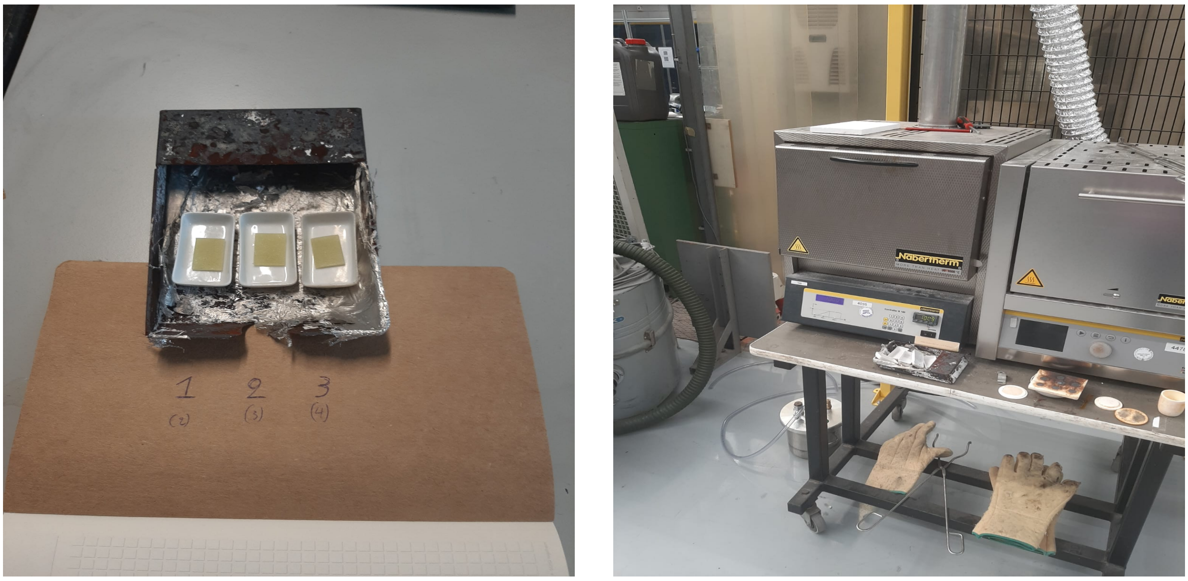
4.7. Composite Quality

This section outlines the standardized procedures for assessing the composition of composite materials, including fiber, matrix, and void contents as per ASTM-D3171-14, ASTM-D2584-7, and ASTM-D2734 standards. It details the sample preparation and the burn-off method for compositional analysis, complemented by optical and scanning electron microscopy for microstructural evaluation. The methodologies employed ensure the precise determination of constituent content, crucial for understanding and enhancing the material's mechanical properties.

4.7.1. Constituent Content

The determination of fiber, matrix, and void content in the manufactured composites was carried out in accordance with the ”Standard Test Methods for Constituent Content of Composite Materials” as defined by ASTM-D31714. This involved the resin burn-off test specified in the ”Standard Test Method for Ignition Loss of Cured Reinforced Resins” (ASTM-D25847) and the ”Standard Test Methods for Void Content of Reinforced Plastics” (ASTM-D2734).

The procedure involved weighing four samples, each with a weight exceeding 1 gram. These samples were then placed in crucibles and subjected to a vacuum furnace set at 595°C for a duration of 4 hours to ensure the complete removal of resin while preventing any ignition. After the heat treatment, the samples were weighed again, representing the mass of the reinforcement remaining in the composite. Some of the samples used and the furnace used for the ignition test can be seen in Figure 4.18



(a) PHTE composite samples used for burn-Off test

(b) Vaccuum furnace used for burning of the resin

Figure 4.18: Constituent content determination through Burnoff test

The different constituent contents were subsequently determined using Equation 4.5 to 4.7, with the density values obtained from the measurements, as explained in subsection 4.4.5.

$$V_f = W_{f_{fraction}} \cdot \frac{\rho_c}{\rho_f} \tag{4.5}$$

$$V_m = W_{m_{fraction}} \cdot \frac{\rho_c}{\rho_m} \tag{4.6}$$

$$V_v = 1 - (V_f + V_m) \tag{4.7}$$

Where :

- ρ_c : Density of the composite
- ρ_f : Density of the reinforcements, taken as 2.7 g/cm^3
- $W_{f_{fraction}}$: Weight fraction of reinforcement
- $W_{m_{fraction}}$: Weight fraction of matrix
- V_v : Void content of the laminate
- V_f : Fiber content of the laminate
- V_m : Matrix content of the laminate

4.7.2. Optical Laser Microscopy

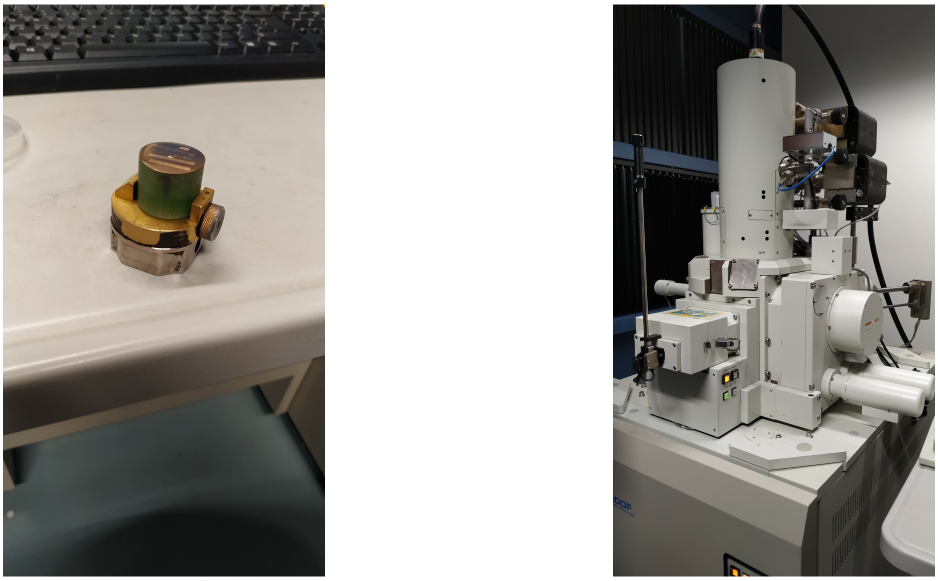
The accuracy of the calculated constituent contents was validated through optical microscopy using the Keyence VK-X1000 3D Laser Scanning Microscope. Four composite samples, extracted from different locations within the laminate, were embedded in Technovit® 4071 epoxy resin at standard mixing ratios. These samples underwent a polishing process using a sequence of sandpaper grits, specifically 400, 800, 1200, 2400, and 3200, with each grit applied for a duration of 2 minutes per step. The polishing was performed using a Tegramin-20 Grinding and Polishing machine.

Subsequently, laser microscopy images were captured at magnification scales of 10x and 20x. These images were later subjected to analysis using ImageJ software, leveraging the voidContentMeasurement.ijm macro to determine the void content within the composite specimens.

4.7.3. Scanning Electron Microscopy

To examine the voids, fibers, and the adhesion between fibers and the fiber-matrix interface, JSM-7500F **S**canning **E**lectron **M**icroscope (**SEM**) was employed. The sample used for laser microscopy was also utilized for SEM analysis. However, in order to facilitate SEM examination, the sample required specific preparation.

This preparation involved the application of an extremely thin layer of gold coating to the sample. The primary objective of this coating process was to establish a conductive layer on the sample's surface. This conductive layer significantly enhances the quality and reliability of the signal that can be detected, thus ensuring more accurate and informative results for subsequent analysis.



(a) Prepared samples for SEM analysis **(b)** JSM-7500F Scanning Electron Microscope

Figure 4.19: SEM samples and microscope used

4.8. Composite Mechanical Testing

The mechanical properties of the composite were examined through tensile testing. The primary objective of these tests was to ascertain whether the manufactured composite adhered to the expected failure modes outlined in the "Standard Test Method for Tensile Properties of Polymer Matrix Composite Materials" - ASTM-D3039-089. The samples for testing were prepared in accordance with this standard, and five tensile specimens were obtained from each of the laminates manufactured using PHTE and Epikure/Epikote04908, following the specified dimensions and techniques detailed in the standard. The exact specimen dimensions can be found in Table 4.4 and 4.5 .

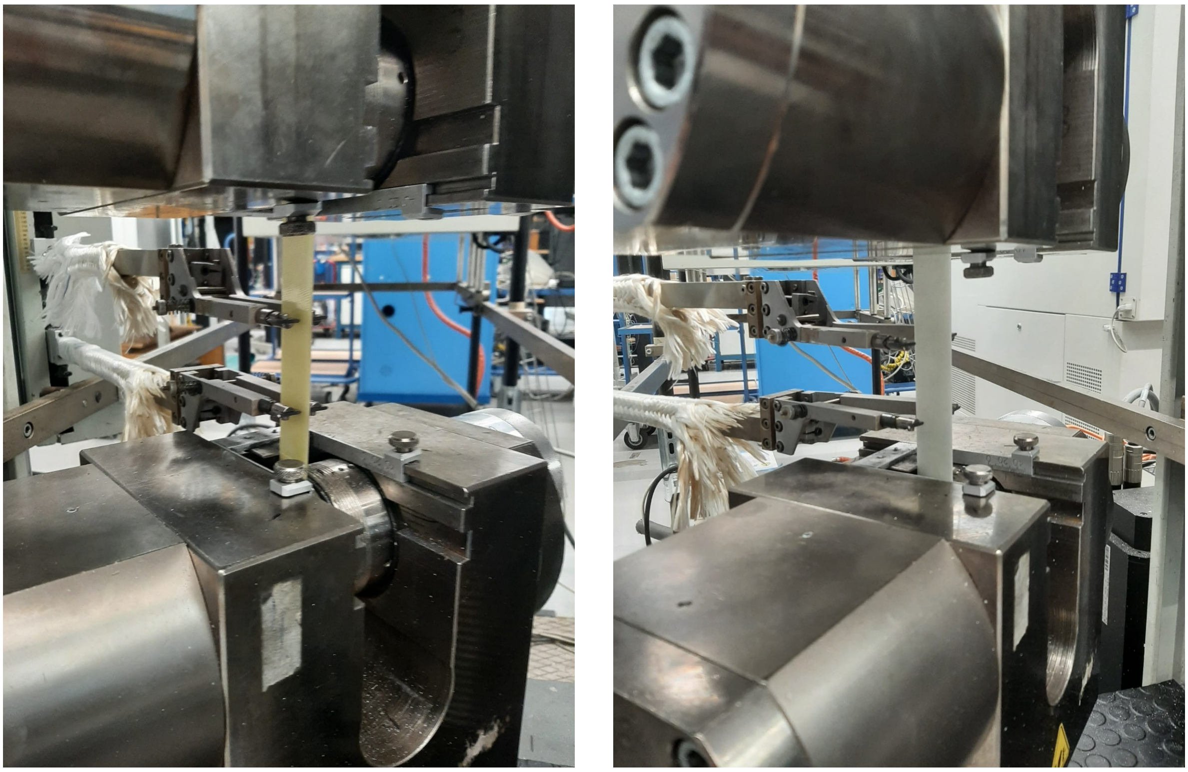
Table 4.4: PHTE-based tensile test specimens' measured dimensions

PHTE/Epikure04908/RD			
Sample	**Width (mm)**	**Thickness (mm)**	**L (mm)**
1	24.91	2.05	250.00
2	24.94	2.02	250.00
3	24.90	1.92	250.00
4	24.86	1.83	250.00
5	24.89	1.97	250.00

Table 4.5: Epikote04908-based tensile test specimens' measured dimensions

Epikote/Epikure04908			
Sample	**Width (mm)**	**Thickness (mm)**	**L (mm)**
1	24.89	2.03	250.00
2	24.86	2.10	250.00
3	24.87	2.01	250.00
4	24.83	2.23	250.00
5	24.84	2.06	250.00

For both the PHTE and Epikote-based composite tests, Zwick and Roell 250 kN tensile machine was employed. The head speed was set at 2 mm/min, and an extensometer was mounted to the structure, as shown in Figure 4.20a and 4.20b. To safeguard the extensometer from damage during specimen fracture, it was removed from the sample once 60% of the expected maximum force was reached. Out of the five tests conducted for each of the two composites, the average values were used to determine the tensile properties.



(a) PHTE/Epikure04908 tensile test configuration

(b) Epikote/Epikure04908 tensile test configuration

Figure 4.20: Tensile test set-up for both PHTE and Epikote based composites

To facilitate a meaningful comparison of the properties of the obtained laminates, it was necessary to normalize the tensile strength and tensile modulus based on a common fiber volume fraction of 60%. This normalization was done using the following equation:

$$NormalizedValue = TestValue \cdot \frac{V_{normalizing}}{V_{specimen}} \tag{4.8}$$

Where :

- $V_{normalizing}$: chosen common fiber volume (volume fraction or %)
- $V_{specimen}$: obtained fiber volume of specimen (volume fraction or %)

5

Results and Discussions

This chapter offers an exploration of the bio-based benzoxazine monomers, covering their synthesis, functional properties, and potential applications. It also delves deeply into the critical aspect of the curing behavior of these monomers, essential for their practical use. The investigation extends to PHTE, with an examination of its properties, structural characteristics, and behavior under various test conditions. Mechanical testing provides insights into its strength, flexibility, and other important attributes. Additionally, the chapter scrutinizes the quality of the resulting composite, including void content and fiber adhesion, providing a holistic view of the material's performance.

Through this chapter, a thorough understanding of the empirical findings of the research is gained. Their significance and their broader implications in the field of sustainable materials science are described.

5.1. Benzoxazines

In this section, the issues connected with the synthesis of the benzoxazine monomers, the obtained monomers, and their bio-content are presented. A range of mono-functional, bis-functional, and tri-functional benzoxazine monomers, each synthesized using different bio-based phenols, amines, and aldehydes, was obtained. Their curing behaviors, which are crucial for their application in composite manufacturing, were also examined. Despite encountering challenges such as brittleness and curing inconsistencies, this investigation sheds light on the complexities and possibilities of bio-based benzoxazines, paving the way for further development in this promising field.

5.1.1. Obtained Bio-Based Benoxazine Monomers

Following the synthesis steps described in subsection 4.2.2 and using the different pre-cursors considered, several different bio-based benzoxazine monomers were obtained. Following the multi-functionality of the used amines, mono-functional, bis-functional, and tri-functional monomers were synthesized. In Table 5.1 the abbreviation used for each monomer, the used precursors, and the bio-content are summarised. The bio-content was calculated based on the initial weight of each pre-cursor used and the percentage of bio-content that each pre-cursor had.

Table 5.1: Sample names, pre-cursors used and achieved bio-content for the synthesized benzoxazine monomers

Sample Name	**Phenol**	**Amine**	**Aldehyde**	**Bio content (%)**
BG1	M-guaiacol	Furfurylamine	Paraformaldehyde	78
BG2	M-Guaiacol	DDS	Paraformaldehyde	40
BG2	M-Guaiacol	T403-Jeffamine	Paraformaldehyde	37
BS1	Sesamol	Furfurylamine	Paraformaldehyde	77
BS2	Sesamol	DDS	Paraformaldehyde	42
BS3	Sesamol	T403-Jeffamine	Paraformaldehyde	39

In Figure 5.1 , the synthesized monomers and the phenol and amine used can be seen. One of the main observations made is that most of the synthesized monomers are found in a solid state, with only the tri-functional monomer based on sesamol being found in a liquid form. This observation is in accordance with findings in the literature, where, in most cases, the obtained mono-functional monomers were found in the form of solid crystals, while the higher functionality ones were typically found in a liquid form.

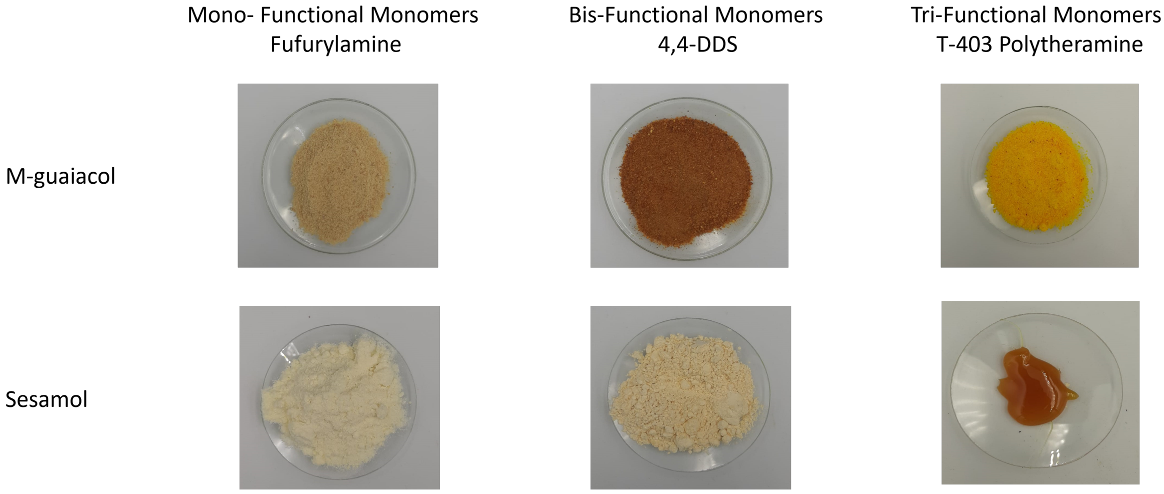


Figure 5.1: Synthesized bio-based Benzoxazine monomers

5.1.2. Curing of Initial Monomers

Prior to conducting additional tests on the synthesized monomers, it was important to establish whether they could be cured in a manner suitable for composite manufacturing. For that, initially, optical inspection was performed using a hot bench of a Koffler system. The Kofler bench was used for assessing the thermal behavior of benzoxazines. Small quantities of the samples were placed on the metal strip with a controlled temperature gradient that ranges from RT to 300°C as shown in Figure 5.2. The strip is designed so that the temperature increases linearly along its length.

The initial results from the Koffler test indicated a rapid change in the state of the sample at temperatures exceeding 240°C. For solid samples, a transition to the liquid state was observed at temperatures exceeding 100°C. The samples were left on the bench for an extended period while being regularly monitored every hour to visually assess whether curing occurred. Surprisingly, even after a full day of exposure to the test conditions at temperatures below 180°C, no curing was observed.

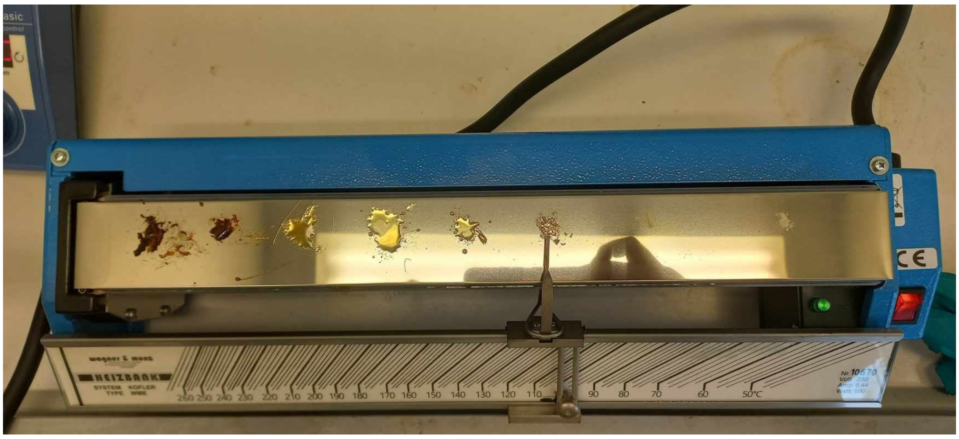


Figure 5.2: Koffler test used for determining optically the curing behavior of benzoxazines

In the temperature range of 180-220°C, the potential for curing was noted, albeit with distinct timelines and effects. Curing was first observed at 220°C after only approximately 2 hours, while at 180°C, it took more than approximately 10 hours for curing to become apparent. It's worth noting that these observations were made visually, and without further testing, the full extent of curing or whether it occurred properly at these temperatures cannot be ascertained. These tests serve as an initial indicator for evaluating the curing behavior of the synthesized monomers depicted in Figure 5.1.

The chosen approach involved placing each monomer in a vacuum oven at 220°C for 4 hours to eliminate any volatiles and trapped gases, following the Koffler test procedure. This method provided insights into the expected behavior of each polymer corresponding to its respective monomer, offering an early assessment of the suitability of each monomer for use in combination with reinforcements. The results of these tests are shown in Figure 5.3.

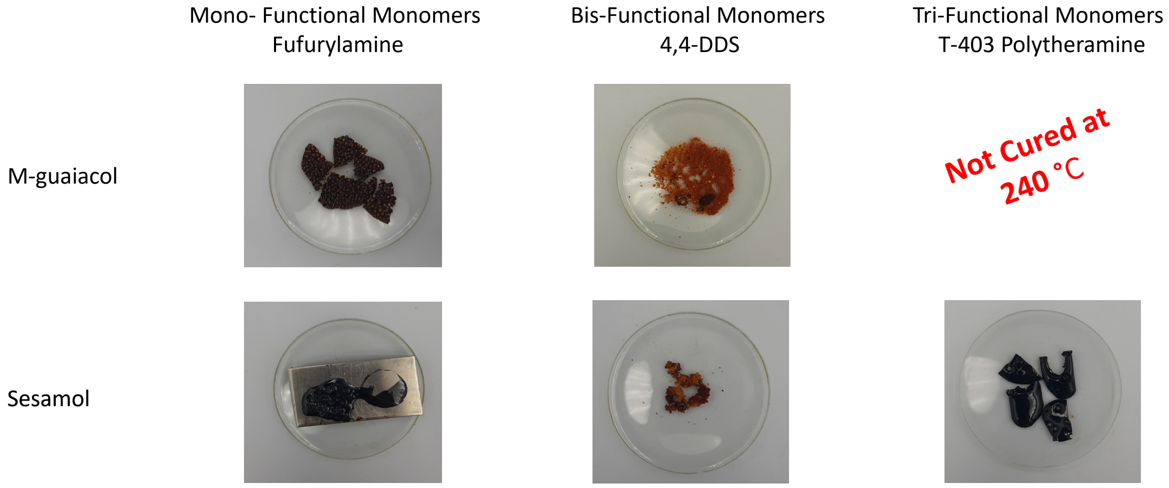


Figure 5.3: Cured Benzoxazines at 220 °C for 4 hours

From the observed images, it is evident that challenges arose during the attempt to cure the monomers.

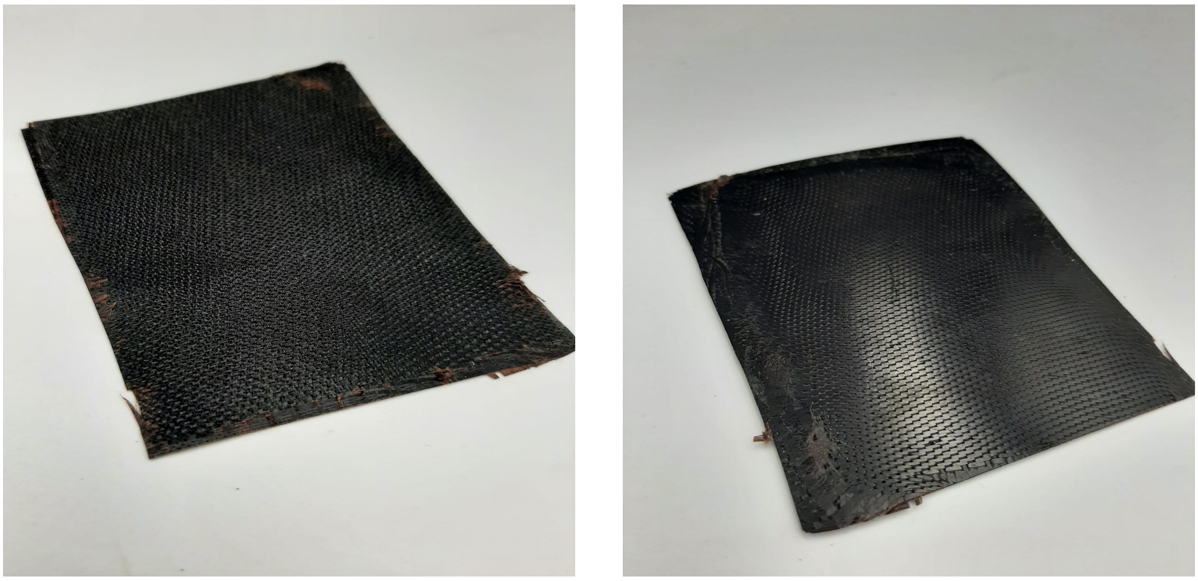
- **M-Guaiacol + Jeffamine (BG3) :** No curing was observed in the monomer containing T-403 Jeffamine, even after incrementally raising the temperature from 220 to 240°C.

- **4,4-DDS-Based Monomers (Bis-Functional Monomers BG2 and BS2) :** Curing was observed in the form of small polymer spheres. It appears that the temperature window for polymerization is extremely narrow, resulting in rapid polymerization and limited flow of the monomeric chain.

- **Furfurylamine-Based Monomers (BG1 and BS1) :**Both the M-guaiacol and Sesamol samples exhibited signs of curing. Sample BG1 displayed a honeycomb-like structure with significant entrapped air. As a result, the resulting polymer exhibited high brittleness, indicating that it may not be suitable for further investigation. Similarly, even though the polymer did not contain as much entrapped air, sample BS1 (comprising Sesamol and Furfurylamine) displayed remarkably high brittleness, despite appearing to be properly cured.

- **Tri-functional Sesamol (BS3):**As evident from the image mentioned earlier, the tri-functional Sesamol monomer emerged as the most promising candidate, showing signs of curing without the presence of volatiles. Nevertheless, it's worth noting that this polymer still exhibited a notable degree of brittleness, even though to a lesser extent when compared to the other samples.

The determination of proper curing conditions for benzoxazine monomers was found to be quite challenging. Even in the initial stages, before proceeding with more detailed chemical and mechanical characterization, it was quite clear that the obtained monomers would perform poorly and would not be useful for composite manufacturing. This was also evidenced by one initial test in which an attempt was made to combine sample BS3, which, as previously mentioned, seemed to be the most promising one, with HEXFORCE 7581. Two laminates, with $[0, 90, 0, 90]_s$ and [0,90,90,0], measuring 5 cm x 10 cm each, were manufactured using the hand layup technique to simply investigate the quality of composites using the benzoxazine resin, as can be seen in Figure 5.4a and 5.4b respectively. The two laminates were cured in a vacuum oven over 220 °C for 4 hours, given the initial curing behaviour observations .



(a) Small laminate $[0, 90, 0, 90]_s$ based on B3

(b) Small laminate [0,90,90,0] based on BS3

Figure 5.4: BS3 [0,90,90,0] laminates obtained using hand layup

Several issues were encountered during and after these trials:

1. **Viscosity of BS3 :** The viscosity of BS3 posed challenges for both spreading and adequate impregnation. To lower the monomer's viscosity, the beaker containing it was subjected to a heat bath at 60°C. Despite this effort, when the monomer came into contact with the low-temperature fibers, impregnation still remained problematic. The initial rheology analysis confirmed the high viscosity of the BS3 monomers. At room temperature, the viscosity exceeded 100 $\text{Pa} \cdot \text{s}$, which was significantly higher compared to the viscosity of commercial Bisphenol F, which exhibited a viscosity of nearly 3 $\text{Pa} \cdot \text{s}$ at room temperature. However, as the temperature increased and reached above 80°C, the viscosity of the sample significantly decreased as can be seen in Figure 5.5.

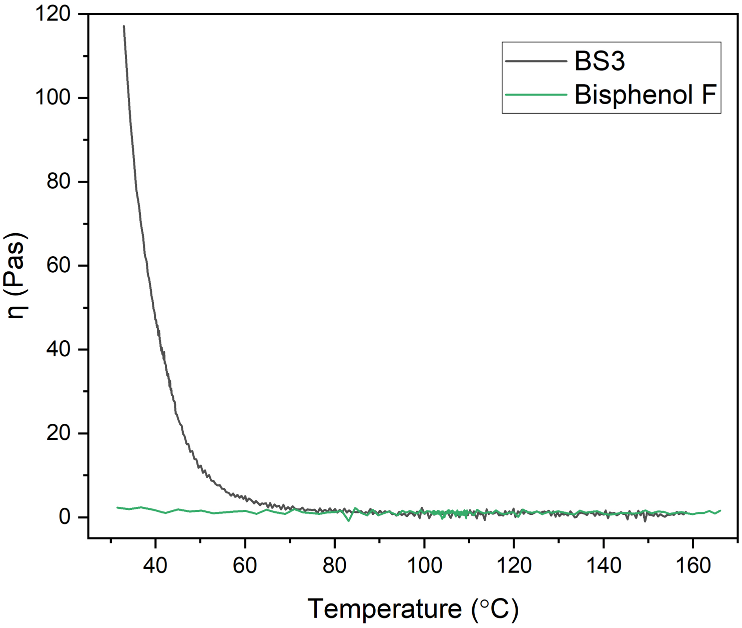


Figure 5.5: Viscosity of BS3 over temperature

2. **Compaction of layers :** The pronounced brittleness of the polymer led to a laminate that was susceptible to delamination. Despite an initial impression of proper curing and well-compacted layers in one of the laminates, delamination began to occur upon simply bending the laminate by hand. It's worth noting that these issues could potentially be addressed by identifying the optimal curing cycle and enhancing the manufacturing technique employed.

3. **Dry Spots :** Visual examination of the manufactured laminate revealed the presence of multiple dry spots on the surface. These dry spots can be easily identified in Figure 5.4. Given that the monomer's viscosity decreased with increasing temperature, it is anticipated that the applied vacuum resulted in a substantial amount of squeeze-out. Once again, it's worth noting that this issue could potentially be resolved by identifying a more appropriate manufacturing technique.

4. **Color of the Laminate :** While not as critical, the coloration of the resulting polymers presents challenges when it comes to their integration into composites. This could make visual inspection of the fabricated structures more challenging. Similarly, complications arose when attempting to examine the fabricated structures using optical laser microscopy. Although the sample used for laser microscopy preparation was of lower quality and didn't yield accurate readings, it was still valuable for assessing the feasibility and challenges associated with the color of the benzoxazine resin. In Figure 5.6, one optical image of the fabricated laminates is displayed. In the highlighted area of the given image, which is a resin-rich area the identification of the fiber bundles compared to the resin is significantly difficult, even after use of corresponding software for analysis. It's important to mention that at even higher magnification and resolution, distinguishing voids from resin-rich areas could sometimes be challenging due to the color of the cured monomers.

Figure 5.6: Laser Microscopy image of BS3-based laminate

Thermal stability was assessed for both sample BS1 and sample BS3 using thermogravimetric analysis to confirm the high thermal stability of the synthesized benzoxazines. The findings indicated that these materials exhibited substantial thermal stability up to temperatures ranging from 200 to 250°C. Beyond this temperature range, approximately 50% of BS3 began to degrade, and this degradation continued up to 500°C. At temperatures exceeding 500°C, a secondary degradation process occurred, albeit at a significantly slower rate. Since the primary focus of this analysis was to demonstrate the high thermal stability of the resins, the experiments were conducted up to lower temperatures (25-700°C), and the final yield was not determined. The obtained thermograph for BS3 is shown in Figure 5.7.

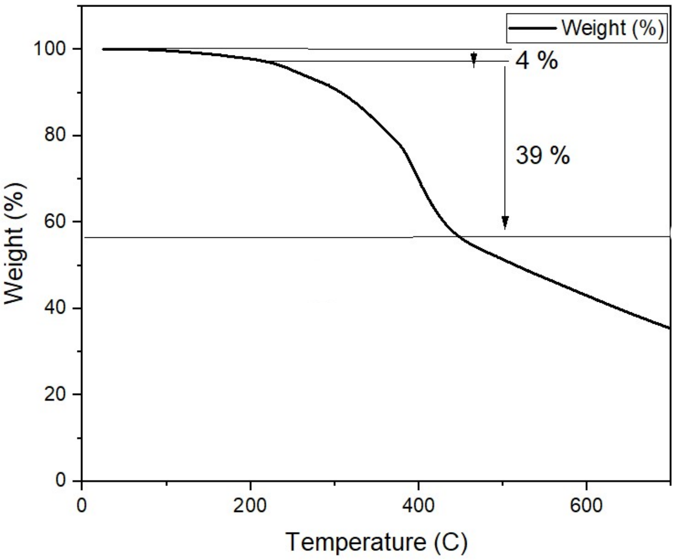


Figure 5.7: BS3 Thermogram from 25 - 700 °C

From the findings mentioned above, it was determined that obtaining high bio-content benzoxazines was indeed possible. However, their challenges related to curing behavior and high brittleness could potentially pose significant obstacles in the course of further research. It was observed that out of the six synthesized monomers, only three cured in a manner suitable for composite manufacturing, and even those exhibited notable issues concerning brittleness and coloration. While their high thermal stability was identified, particularly in the case of sample BS3, it was concluded that, given the extensive time invested in synthesis, pursuing an investigation into the curing behavior of benzoxazines to find an optimal solution would likely lead to substantial delays in the study, with no guarantee that the results would prove beneficial for composite structures. Therefore, from that point onward, the research focus shifted towards the bio-based epoxy.

5.2. PHTE

In this section, an investigation into the physical properties of the PHTE/Epikure 04908-reactive diluent resin system is presented. The focus is on the resin's density, gel content, and water affinity, which are critical in assessing its suitability for composite manufacturing applications.

Subsequent analysis delves into the chemical structure using spectroscopic techniques. The rheological behavior is assessed, indicating the resin's processing characteristics, while thermal stability and glass transition temperatures are determined via TGA and DSC analyses.

Lastly, the mechanical properties are evaluated through DMA, tensile, and flexural testing, underscoring the importance of post-curing for optimal material performance. This investigation serves as a foundation for understanding the transformative potential of sustainable resins in composite manufacturing. In Table 5.2 the calculated properties of the PHTE/Epikure04908 system are summarized, over the obtained properties of Epikote/Epikure04908 as derived from the given technical data sheet.

Table 5.2: PHTE/Epikure04908 properties over Epikote/Epikure04908

Property	**Unit**	**EPIKOTE™-Epikure 04908**	**PHTE-Epikure04908**
Density	g/cm3	1.15	1.20
Tensile strength	MPa	74	56 ± 5
Tensile strain	%	9.4	3.6
Modulus in tensile	MPa	2900	3950 ±273
Flexural strength	MPa	112	80 ± 15
Modulus in flexure	MPa	3100	3590 ± 510
Water absorption after 24h 23 ° C	%	0.18	0.76
Tg	°C	89a	125a, 123b

5.2.1. Density, Gel Content, and Water Affinity

The resin created from the PHTE/Epikure 04908-reactive diluent combination exhibited an average density of 1.2 g/cm^3 at 23°C, as determined by ASTM-D792 and summarised in Table 5.3. In comparison, the technical data sheet specifies a density of 1.15 g/cm^3 for EPIKOTE™-EPIKURE™04908 resin at room temperature. This variation can be attributed to the branched structure of PHTE, which results in a more densely packed polymer system compared to the oligomeric BADGE system. This branched structure of PHTE could lead to a significantly higher degree of cross-linking, increasing that way the density of the system. In addition to that, the existence of the 10% diluent could also have a significant effect on increasing the final density of the system.

It's worth noting that the PHTE resin includes 10 wt.% of a monofunctional epoxy diluent, which reduces the crosslinking density per unit. The gel content, assessed according to ASTM D2765-16 was found to be 99% for the case of the pure resin system and 0.97% for the composite after submersion in toluene for 72 h.

Table 5.3: Density determination or PHTE resin and composite taking the density of air as 0.0012.

Sample	**Auxiliary liquid Temperature (C)**	**Auxiliary liquid density (g/cm3)**	**Dry weight A (g)**	**Wet weight B (g)**	**Density (g/cm3)**
		Resin			
R1	22.2	0.9975	0.3813	0.0626	1.1932
R2	20.6	0.9981	0.5422	0.0943	1.2080
R3	20.6	0.9981	0.6953	0.1182	1.2023
Average					**1.2012**
		Composites			
C1	22.8	0.99761	1.3232	0.5827	1.7817
C2	20.6	0.9981	1.0673	0.4664	1.7719
C3	20.6	0.9981	1.0262	0.4447	1.7605
Average					**1.7714**

After immersing the resin sample in DI water for 24 hours at 25°C, the sample's mass increased by 0.76% as shown in Table 5.5. In a similar fashion, for the case of the composite samples, the mass increased by 0.98%, corresponding to the water absorbance. It can be observed that the absorbance of the samples is happening at a high rate initially while the longer the samples are left submerged in water, the absorbance is reduced.

Table 5.4: Water Absorbance of Resin and Composite Samples

Sample	**Duration of test**	**Start date and time**	**End date and time**	**Dry Mass (g)**	**Wet Mass (g)**	**Percentage increase (%)**
			Resin			
Resin 1	24 hrs	25/07/23, 16:00	26/07/23, 16:12	0.3812	0.3841	0.77
Resin 2	48 hrs	25/07/23, 16:00	27/07/23, 16:11	0.2029	0.2049	0.98
Resin 3	7 days	25/07/23, 16:00	01/08/23, 15:48	0.3089	0.3141	1.34
Resin 4	14 days	25/07/23, 16:00	08/08/23, 16:25	0.5014	0.5108	1.87
			Composite			
Composite 1	24 hrs	25/07/23, 16:00	26/07/23, 16:12	0.3461	0.3495	0.98
Composite 2	48 hrs	25/07/23, 16:00	-	0.3485	-	-
Composite 3	7 days	25/07/23, 16:00	01/08/23, 15:48	0.3619	0.3762	3.95
Composite 4	14 days	25/07/23, 16:00	08/08/23, 16:25	0.4811	0.5020	4.32

The water contact angle was measured for various samples to gain further insights into the resin's hydrophilicity (see Figure 5.8 and 5.9). Among the five samples tested, an average contact angle of 55.2 was recorded, indicating a slight degree of hydrophilicity in the resin system as can be seen in Table 5.5.

Table 5.5: Water Absorbance of Resin and Composite Samples

Sample no	**CA (Left)**	**CA (Right)**	**CA (Average)**
	Resin		
Resin 1	57.54	51.94	54.74
Resin 2	53.07	53.90	53.58
Resin 3	57.88	58.55	58.22
Resin 4	65.94	65.06	65.50
Resin 5	45.26	43.00	44.14
	Composite		
Composite 1	62.63	62.63	62.63
Composite 2	43.21	43.95	43.58
Composite 3	59.20	55.63	57.41
Composite 4	53.72	55.33	54.52
Composite 5	64.23	60.93	62.58

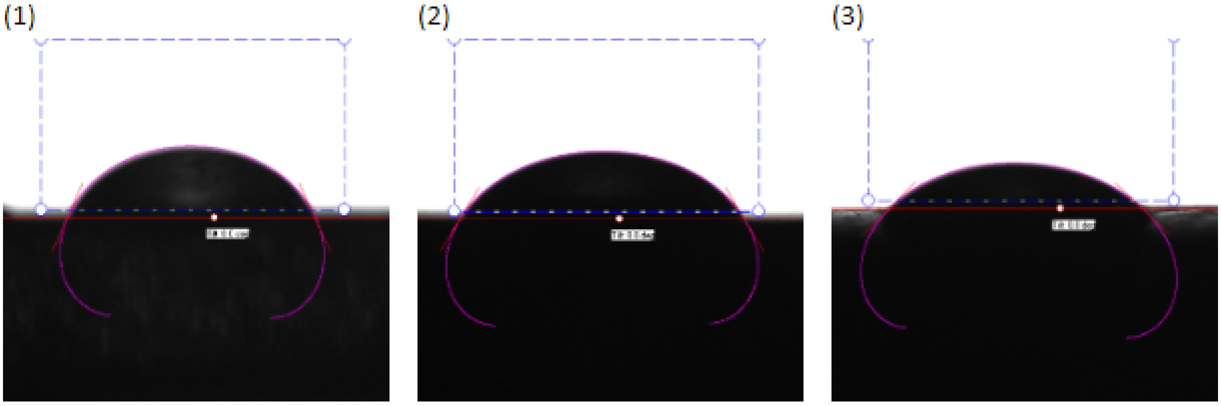


Figure 5.8: Water Contact Angle on PHTE/Epikure04908 resin specimen

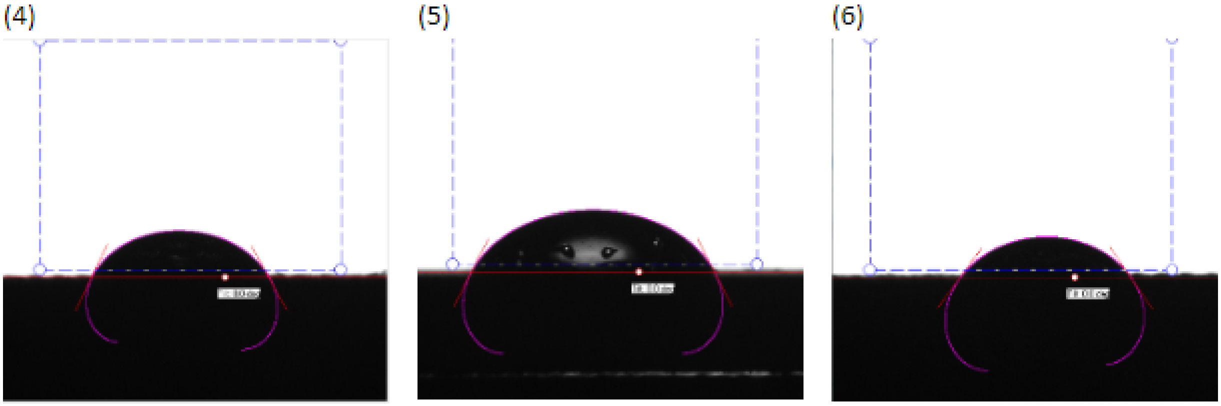


Figure 5.9: Water Contact Angle on PHTE/Epikure04908 composite specimen

5.2.2. H-NMR, C-NMR and FTIR Spectra of PHTE

FT-IR spectra of Epikure04098 and PHTE are presented in Figure 5.10 depicting characteristic signals arising from functional groups (i.e. epoxy, amino, benzene ring), that are useful to monitor during curing reactions. Mid-range infrared (IR) spectroscopy, which spans the range of 550-4000 cm-1, was employed to detect an absorption peak at 907 cm-1 corresponding to the C-O stretching of the oxirane ring. This peak was notably prominent in the PHTE monomer, as depicted in Figure 5.10. In the case of the room temperature (RT) cured sample, a significant reduction in this peak was observed, indicating the progression of the curing reaction. However, post-curing at 140°C completely eradicated the C-O absorption band associated with the oxirane ring. This observation suggests that the curing reaction is not entirely complete at room temperature, aligning with the findings from dynamic mechanical analysis (DMA) .

Ideally, a more comprehensive assessment of the curing process would involve the use of **N**ear-**I**nfrared (**NIR**) spectroscopy, spanning the range of 4000-14000 cm-1. This is because the oxirane ring stretching peak at 4530 cm-1 exhibits minimal overlap with other bond absorption wavelengths. Such a choice allows for a precise determination of conversion, which is challenging with mid-IR spectroscopy due to significant overlapping signals in the 910 cm-1 region.

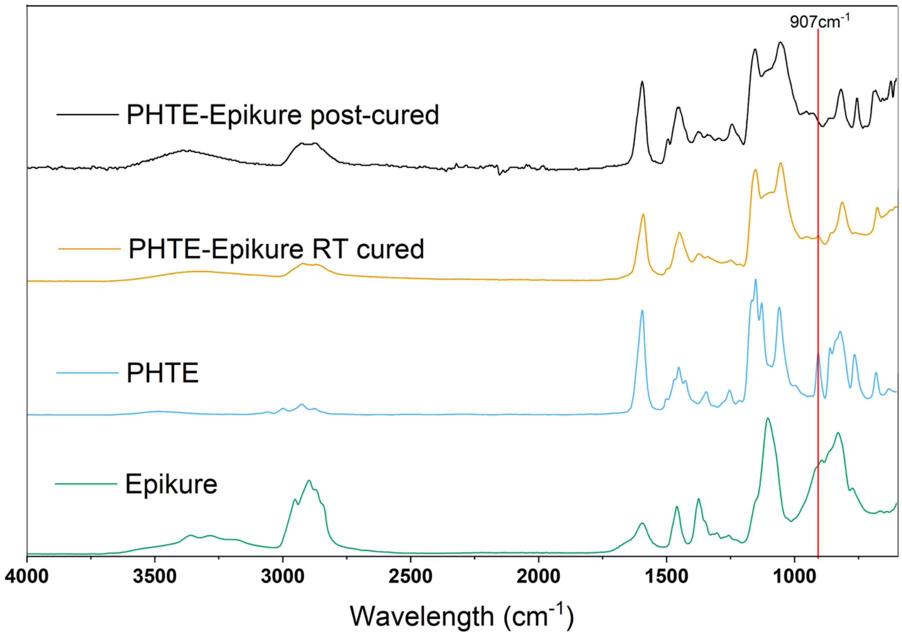
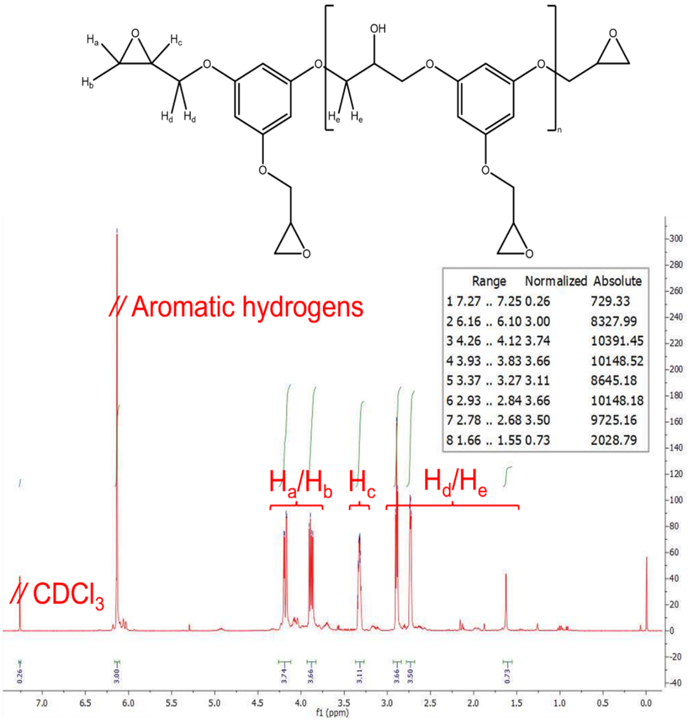


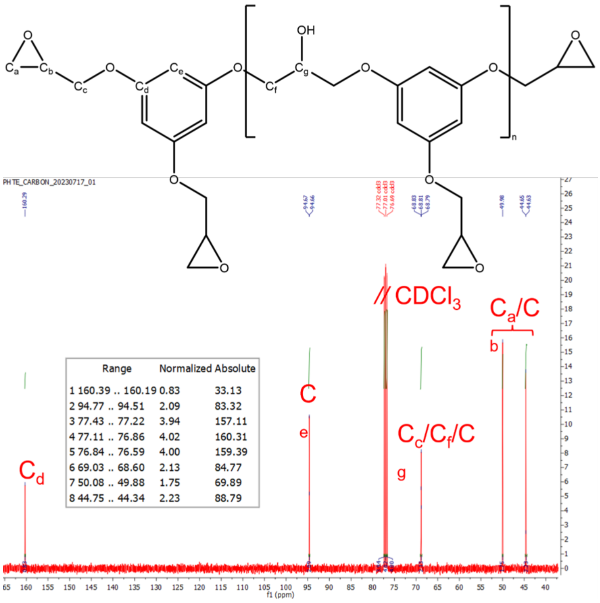
Figure 5.10: FT-IR spectra of PHTE, Epikure, and PHTE/Epikure04908 cured resin systems

Structural analysis of PHTE was investigated using 1H and 13C NMR spectroscopy, which confirms the purity and structure since NMR signals are allocated to the expected chemical structure as can be seen in Figure 5.11a and 5.11b.



	Range	Normalized	Absolute
1	7.27 .. 7.25	0.26	729.33
2	6.16 .. 6.10	3.00	8327.99
3	4.26 .. 4.12	3.74	10391.45
4	3.93 .. 3.83	3.66	10148.52
5	3.37 .. 3.27	3.11	8645.18
6	2.93 .. 2.84	3.66	10148.18
7	2.78 .. 2.68	3.50	9725.16
8	1.66 .. 1.55	0.73	2028.79

(a) H-NMR spectra of PHTE



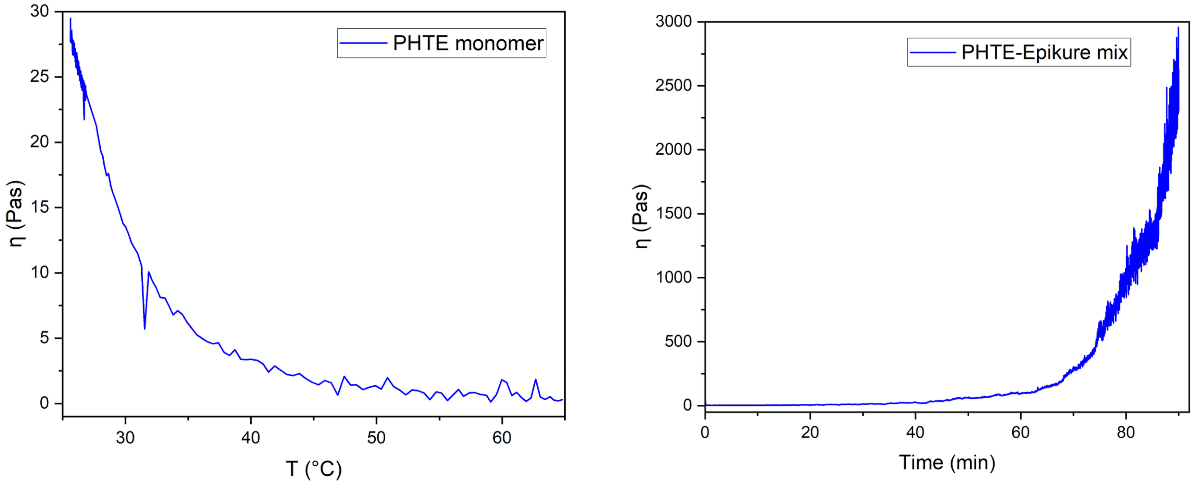
	Range	Normalized	Absolute
1	160.39 .. 160.19	0.83	33.13
2	94.77 .. 94.51	2.09	83.32
3	77.43 .. 77.22	3.94	157.11
4	77.11 .. 76.86	4.02	160.31
5	76.84 .. 76.59	4.00	159.39
6	69.03 .. 68.60	2.13	84.77
7	50.08 .. 49.88	1.75	69.89
8	44.75 .. 44.34	2.23	88.79

(b) C-NMR spectra of PHTE

Figure 5.11: H-NMR and C-NMR spectra of PHTE

5.2.3. Rheology, DSC, and TGA data

The viscosity of pure PHTE was found to be remarkably high, measuring 30 Pa·s at RT, as illustrated in Figure 5.12a. To reduce the viscosity of the mixture, a monofunctional reactive diluent, 1,2-Epoxy-3-phenoxypropane, was introduced, as the addition of Epikure 04098 hardener alone proved insufficient in viscosity reduction. A 10 wt.% concentration of the diluent was used, resulting in a system viscosity of 2 Pa·s shortly after mixing at room temperature as can be seen in Figure 5.12b. This viscosity level is suitable for composite manufacturing using techniques like hand layup and vacuum bagging, though it remains significantly higher than that of Epikote-Epikure 04098, which measures 0.13 Pa·s shortly after mixing. Furthermore, the viscosity of the PHTE-Epikure mixture increases to 30 Pa·s within 43 minutes, indicating a rapid curing time.



(a) PHTE over increasing Temperature

(b) PHTE system over time

Figure 5.12: Rheology findings of PHTE/Epikure04908 2:1 system

The rheology analysis revealed that the gel point time for the system was 197.5 minutes, which was determined as the point where G' and G" intersected, as shown in Figure 5.13, signifying that the resin exhibited more elasticity than viscous characteristics. This theoretically provided a substantial processing window for either a wet layup or vacuum infusion to take place.

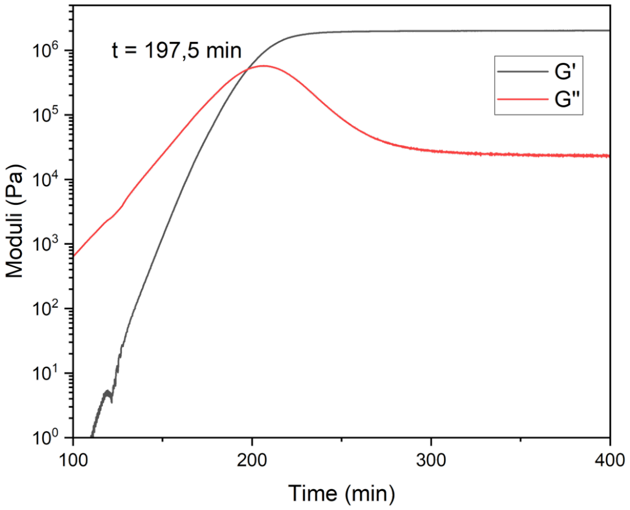
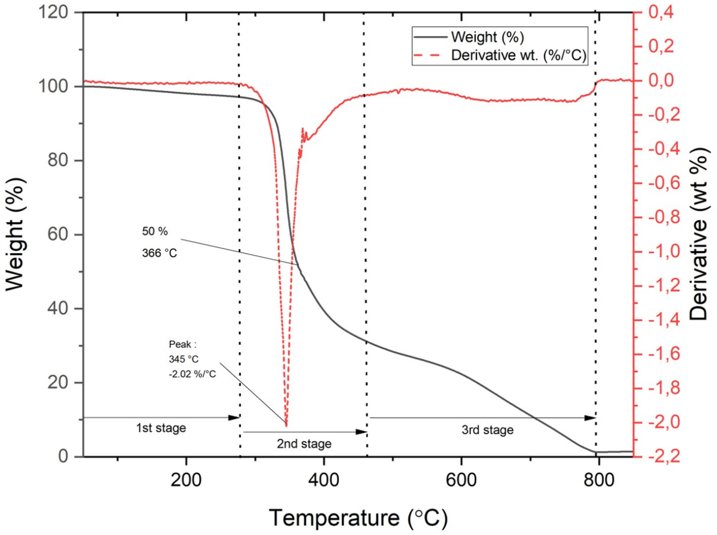


Figure 5.13: Storage (G') and Loss (G") modulus over time

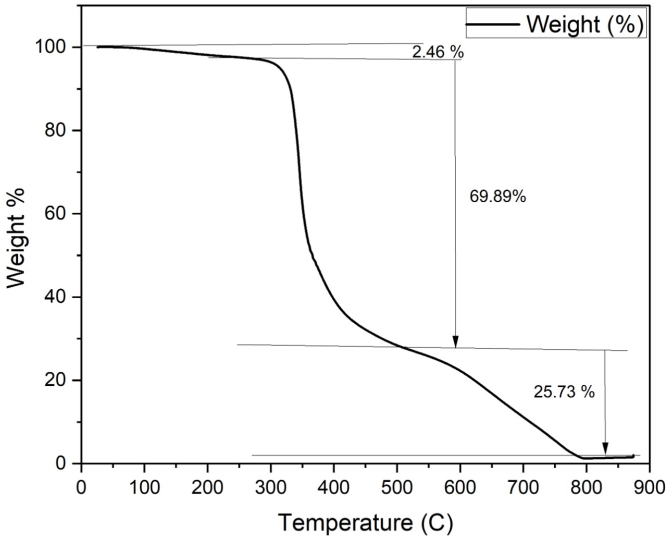
However, it's important to note that the pot life was approximately 40 minutes before significant increases in viscosity were observed. When working with bulk material, the working time was considerably shorter due to a lower surface area to volume ratio, resulting in more trapped heat from the exothermic reaction and consequently faster reaction times. In this case, as was mentioned in section 4.6 a critical mass of approximately 40 g was determined, and the material solidified in approximately 5 minutes using the specific apparatus.

This pot life finding stands in contrast to the reference system using Epikote/Epikure04908, which exhibited a pot life of 300 minutes. It's worth noting that Epikote is a BADGE-based system with an epoxy-to-phenyl ratio of 1:1, while the PHTE-based system has a ratio of epoxy-to-phenyl of 3:1, which may account for the differences in pot life observed.

In Figure 5.14 the thermogravimatrIC analysis performed on the resin system is shown.



(a) TGA and DTG diagram of PHTE/Epikure04908 system

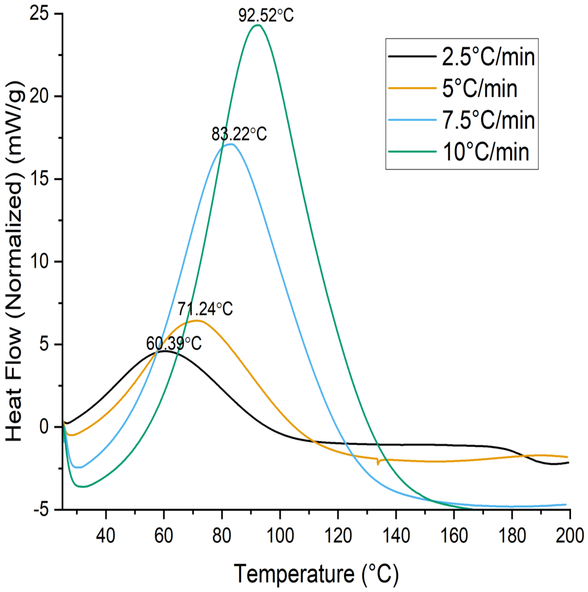


(b) TGA diagram of PHTE/Epikure04908 system

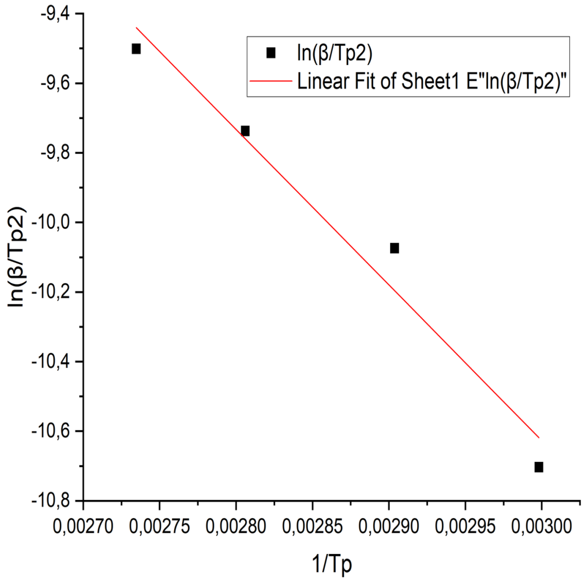
Figure 5.14: Thermograph of PHTE-Epikure04908 2:1 system from 25 to 900 °C with 10 °C/min heating rate

The thermogravimetric analysis (TGA) measurements showed that the cured resin system exhibited high thermal stability up to 320°C. Beyond this temperature, approximately 50% of the resin degraded within a 40°C range, as was observed in the TGA and **D**ifferential **T**hermogravitometry (**DTG**) diagram in Figure 5.14a. At temperatures exceeding 460°C, a secondary degradation process took place, leaving almost no remaining mass at 800°C, indicating a low char yield.

Differential Scanning Calorimetry signified a glass transition temperature of the resin system at 123 °C. The calculated activation energy (Ea) of the curing reaction was determined to be 37.2 kJ mol^{-1}, as detailed in Figure 5.15a and 5.15b. This Ea value falls on the lower end for epoxy-amine reactions, suggesting that the curing process is relatively fast.



(a) DSC runs for PHTE-Epikure04908 mix in 2:1 ratio at different heating rates

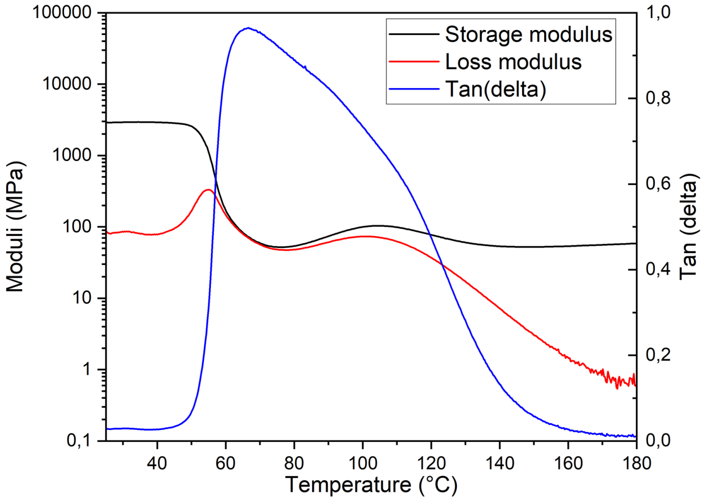


(b) Linear fit using Kissinger model to determine the activation energy of the curing reaction

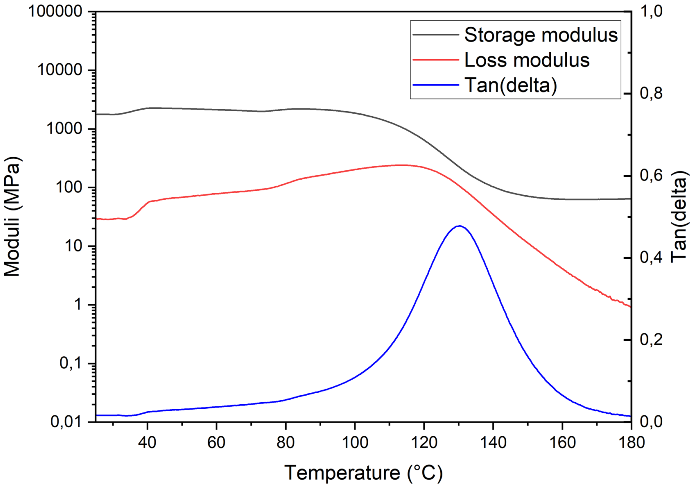
Figure 5.15: DSC analysis performed on PHTE/Epikure04908 system

5.2.4. Mechanical Testing of Resin

The DMA analysis conducted on pure resin samples, which were cured at room temperature, revealed an initial storage modulus (E') of 2000 MPa and a loss modulus (E") of 80 MPa at room temperature. During the first heating cycle, an initial glass transition temperature (T_g) of 60°C was observed, indicated by the peak of tanδ as can be seen in Figure 5.16a. Subsequently, the T_g increased to 125°C following a post-curing step at 140°C for 1 hour, as shown in Figure 5.17a. Therefore, based on the DMA data, it was determined that post-curing was necessary to fabricate a fully crosslinked resin. As a result, post-curing was implemented in all PHTE resin formulations throughout this study.



(a) PHTE-Epikure04908 system cured at RT

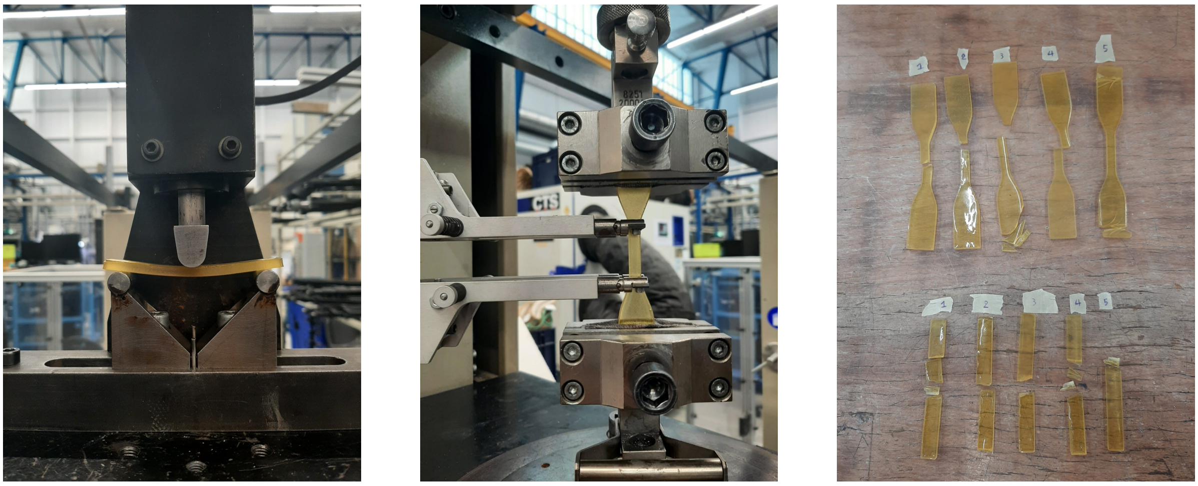


(a) PHTE-Epikure04908 system post cured at 140 °C for 1 hour

Figure 5.17: DMA curves of PHTE-Epikure04908 2:1 system

The flexural and tensile properties of the respective samples were determined by calculating the average from the results of five tests. Notably, during the tensile tests, grip-related failures were observed in two out of the five specimens, specifically specimens 3 and 5. An investigation was conducted on the failed samples to ascertain whether surface quality played a role in the failures. Manufacturing records indicated that the surfaces were both flat and parallel.

In the case of specimen 3 (TR3), it was discovered that a small fragment of specimen 2 (TR2), which had previously failed, remained inside the clamp. Upon contact with specimen 3, this fragment could potentially generate high stresses, leading to the failure seen in the grip/tab failure. In Figure 5.18c all the different specimens after failure can be seen.



(a) Flexural testing of resin

(b) Tensile testing of resin

(c) Specimens after failure

Figure 5.18: Digital images of mechanical tests and PHTE specimens in the testing equipment and after failure

As was mentioned the grip/clamp failure can be observed on specimens 3 and 5 of the tensile specimen. Consequently, the data obtained from these specimens could not be utilized to determine the tensile strength and modulus of the resin. Table 5.6 and 5.7 provide a summary of the results from the flexural and tensile tests on the resin. For the determination of the tensile stiffness of the material, the readings from the extensometer attached to the neck of the dog bones were used. The stress at 0.05%

and 0.25% strain was used.

Table 5.6: Results of Flexural testing of PHTE resin

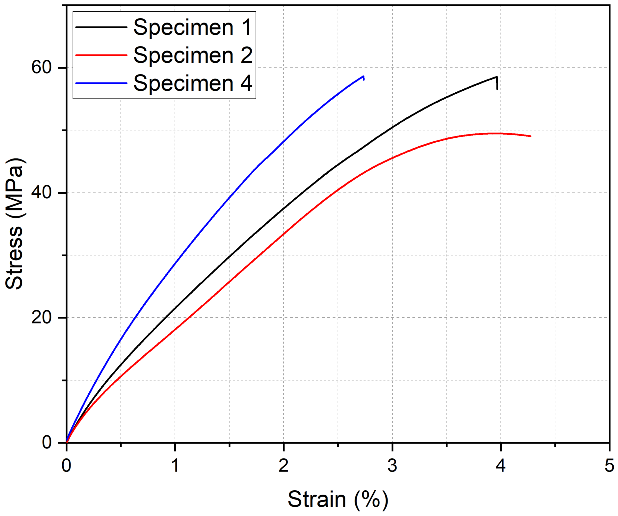
Sample	Maximum Force (N)	Flexural Strength (MPa)	Flexural Modulus (MPa)
FR1	167	94	4011
FR2	127	70	3671
FR3	197	92	4070
FR4	130	85	3559
FR5	101	59	2803
Average (MPa)	144	80	3622
Standard Deviation (MPa)	38	15	507

Table 5.7: Results of Tensile testing of PHTE resin

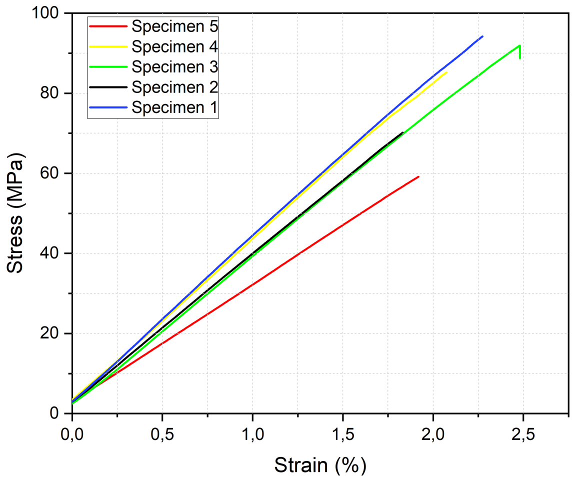
Sample	Maximum Force (N)	Tensile Strength (MPa)	Tensile Modulus (MPa)	Tensile Strain (%)
TR1	1405	59	3910	3.965
TR2	1188	50	3688	4.274
TR4	1408	59	4231	2.736
Average (MPa)	1334	56	3943	3.658
Standard Deviation (MPa)	126	5	273	0.814

In accordance with ISO178 standards, the cured resin exhibited a flexural strength of 80 MPa and a flexural modulus of 3600 MPa, as illustrated in Figure 5.19b and Table 5.6. The standard deviation from these values for different specimens was calculated to be 15 MPa for flexural strength and 507 MPa for flexural modulus, as depicted in the stress-strain curve in Figure 5.19b.

Regarding the tensile tests, from the three usable samples, a tensile strength of 56 MPa and a tensile modulus of 4000 MPa were obtained, with a total strain of 3.6 % in accordance with ASTM-D638, as illustrated in Figure 5.19a . The standard deviation for these values was calculated to be 5 MPa for tensile strength and 273 MPa for tensile modulus, as shown in the stress-strain curve in Figure 5.19a.



(a) Stress-Strain Curve of Tensile Testing of PHTE system



(b) Stress-Strain Curve of Flexural Testing of PHTE system

Figure 5.19: Stress-strain curves obtained through tensile and flexural testing of PHTE resin

Comparing the PHTE resin to the Epikote/Epikure04908 system, which does not include diluent, it's evident that the PHTE resin exhibits a significant increase in stiffness in both tensile and flexural properties. However, this increase in stiffness comes at the cost of a 24 % reduction in tensile strength and a 29 % reduction in flexural strength. These results demonstrate that the PHTE resin results in a stiffer yet more brittle system when compared to the BADGE reference with its initial formulation.

In order to facilitate a more meaningful comparison, it was deemed that both mechanical tests should be performed on samples based on Epikote/Epikure04908, including 10 % diluent. Five flexural and five tensile samples were manufactured following the instructions in the standards and the properties of the respective samples were determined by calculating the average from the results of the tests. In Table 5.8 and 5.9 the calculated results of each test are summarized. Sample TR2e experienced a failure at a substantially lower force compared to the other specimens, possibly due to the high clamp force needed to prevent any slippage. Consequently, the data from that particular specimen were excluded from the property determination.

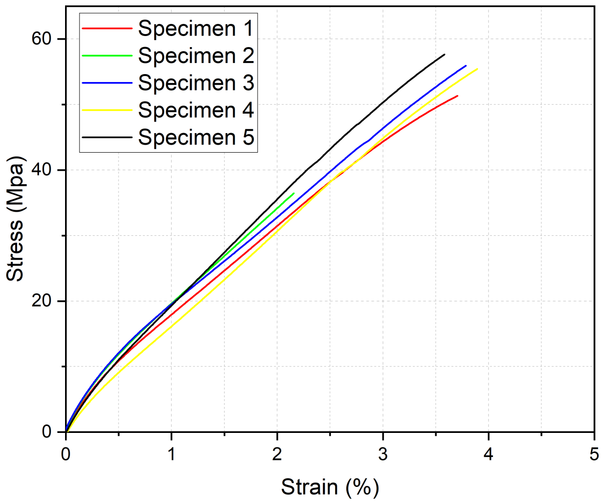
Table 5.8: Results of Flexural testing of Epikure/Epikote resin

Sample	**Maximum Force (N)**	**Flexural Strength (MPa)**	**Flexural Modulus (MPa)**
FR1e	97	56	3480
FR2e	93	51	3380
FR3e	99	54	3830
FR4e	86	54	3220
FR5e	102	58	3880
Average (MPa)	95.4	54	3558
Standard Deviation (MPa)	5.5	2.5	287

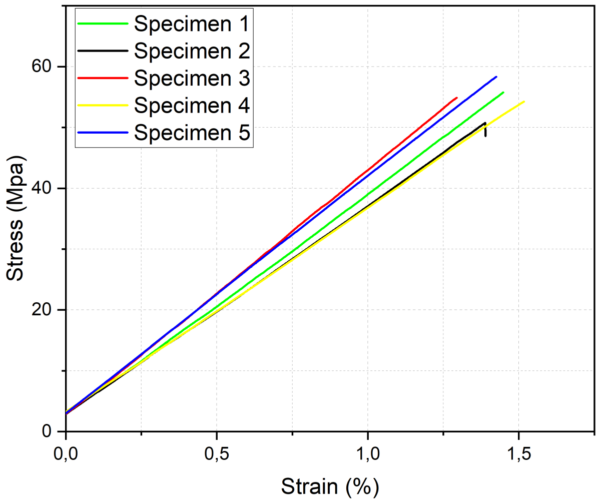
Table 5.9: Results of Tensile testing of Epikote/Epikure resin

Sample	**Maximum Force (N)**	**Tensile Strength (MPa)**	**Tensile Modulus (MPa)**	**Tensile Strain (%)**
TR1	1263	51	4189	3.708
TR3	1377	55	4415	3.785
TR4	1312	55	3668	3.894
TR5	1364	57	2802	3.583
Average (MPa)	1329	55	3769	3.743
Standard Deviation (MPa)	52	3	716	0.131

Compared to the data from the technical data sheet, the cured resin, including 10% diluent, exhibited a flexural strength of 54 ±3 MPa and a flexural modulus of 3500±300 MPa, as illustrated in Figure 5.20b and Table 5.8. Regarding the results from the tensile test, a tensile strength of 54.5 ±2.5 MPa and a tensile modulus of 3770± 716 was determined.



(a) Stress-Strain Curve of Tensile Testing of Epikote system



(b) Stress-Strain Curve of Flexural Testing of Epikote system

Figure 5.20: Stress-strain curves obtained through tensile and flexural testing of Epikote/Epikure system with 10% diluent

From the above, it can be observed that both the flexural and the tensile properties of the PHTE resin system are comparable to those of the Epikote/Epikure04908 including the diluent. The strength of the Epikote system decreases significantly with the addition of the diluent in the formulation.

5.3. Composite Quality

The initial fiber volume fraction, matrix volume fraction, and void content of the PHTE-based laminate were determined, following ASTM D3171-99 and ASTM D2734-94, to be 42.21%, 51.88%, and 5.91%, respectively as shown in Table 5.10. The presence of a relatively high void content is ascribed to both the reactive nature of PHTE and manufacturing defects associated with the hand layup method used. An increase in viscosity after 40 minutes resulted in difficulties with impregnation.

Table 5.10: Fiber, Matrix, and Void content obtained through Resin Burn-off test and through optical microscopy analysis for the PHTE-Epikure-1,2-Epoxy-3-phenoxypropane glass fiber composite

							Fiber, Matrix and Void content through Resin Burn-off						
	Before Burnoff	**After Burnoff**					**PHTE based Laminate**				**Epikure/Epikote based Laminate**		
Sample	**Sample Mass (mg)**	**Dry Mass (mg)**	**Wm (mg)**	**Wff**	**Wmf**	**Td (g/cm3)**	**Vf**	**Vm**	**Vv (burnoff)**	**Vv (microscopy)**	**Vf**	**Vm**	**VV**
1	1518.8	994.4	524.4	0.65	0.34	1.48	0.42	0.50	0.08	0.04	0.45	0.43	0.12
2	1026.8	659.0	367.8	0.64	0.35	1.50	0.41	0.52	0.07	0.04	0.44	0.46	0.10
3	1067.5	691.8	375.7	0.64	0.35	1.49	0.42	0.52	0.06	0.04	0.43	0.47	0.10
4	890.9	588.6	302.3	0.66	0.33	1.48	0.43	0.50	0.07	0.05	0.44	0.46	0.10
Average						1,49	0.42	0.51	0.07	0.04	0.44	0.45	0.11

Verification of the void content was carried out by optical laser microscopy, capturing images from different areas of the manufactured laminate as can be seen in Figure 5.21. Microscopic analysis revealed a void content of 4.71% (see Table 5.10). Notably, there is a 1% difference between the actual void content and the value obtained from microscopy analysis. It's worth noting that some of these voids are sizable, with dimensions as large as 1000 m, which could potentially initiate cracks within the composite material.

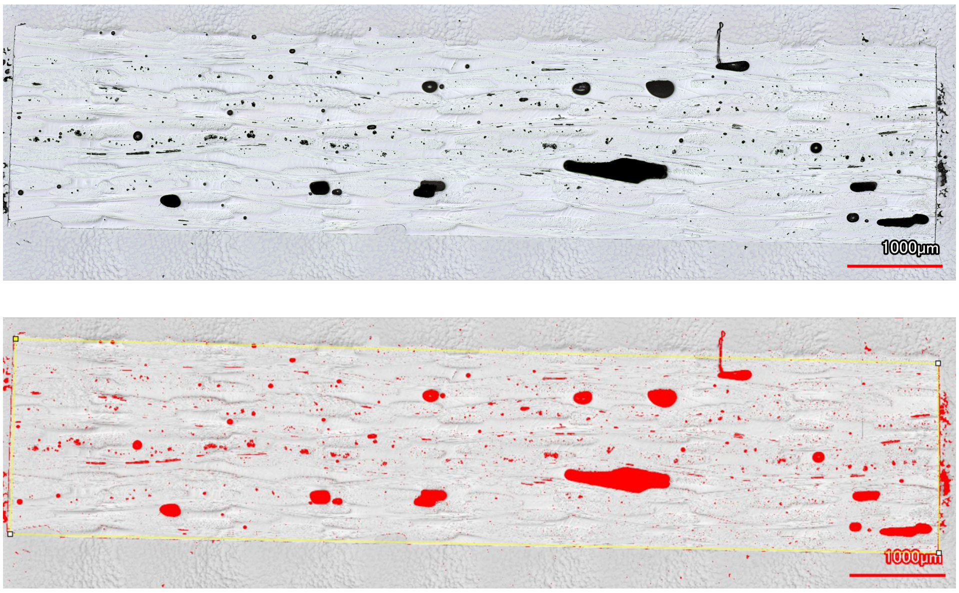


Figure 5.21: Laser microscopy images of the composite and analyzed images through ImageJ software by altering the threshold to obtain void content.

Scanning Electron Microscopy (SEM) images were captured to visually assess how the resin adhered to the fibers. These images revealed that, in some instances, voids were observed around individual fibers, as can be seen in Figure 5.22. The aforementioned variance between the burnoff obtained and the software-obtained contents may be attributed to the presence of these micro-voids within the composite material surrounding bundles of fibers that the analysis software could not identify. However, the investigation did not specifically examine the adhesion of the resin to the fibers.

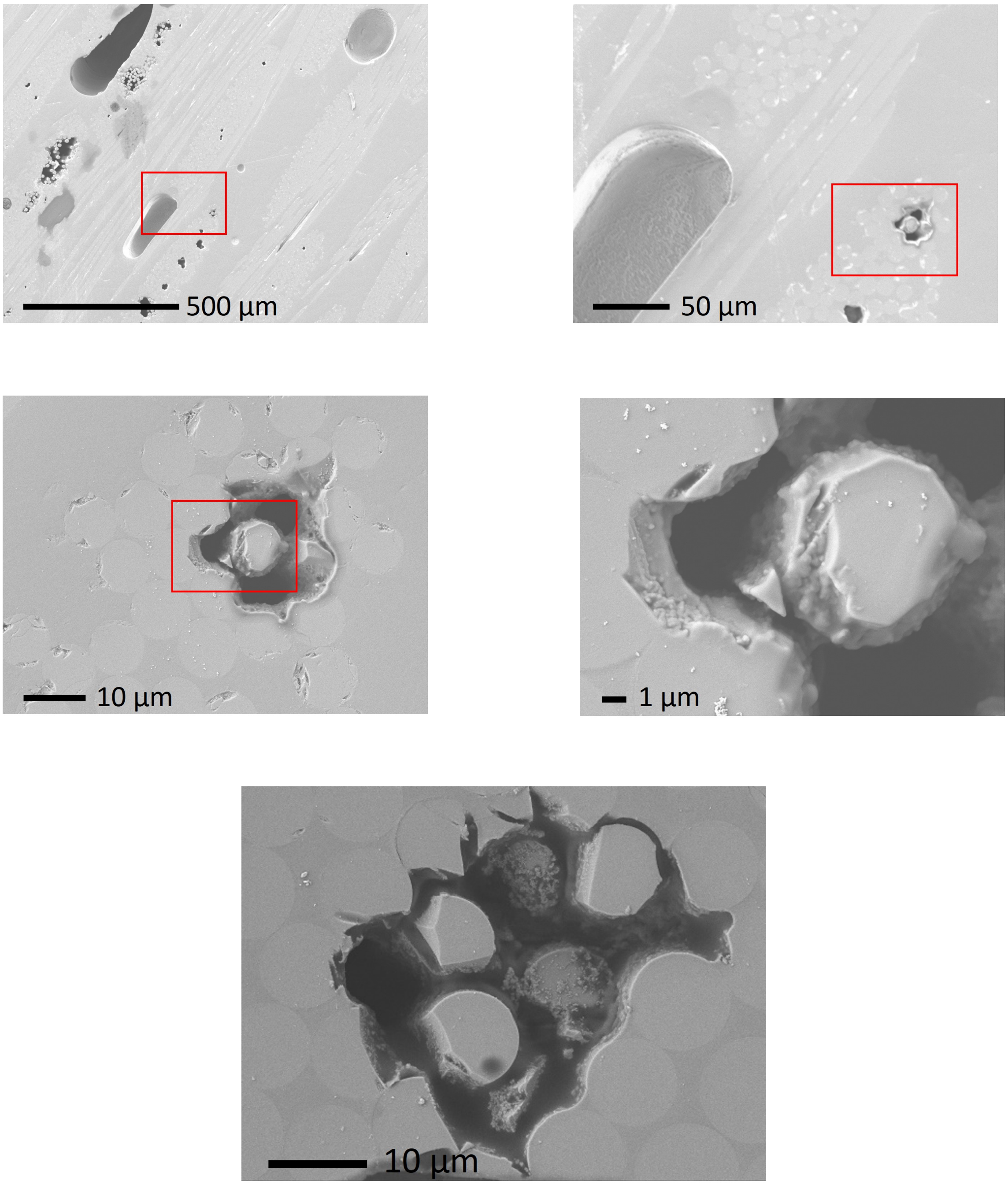
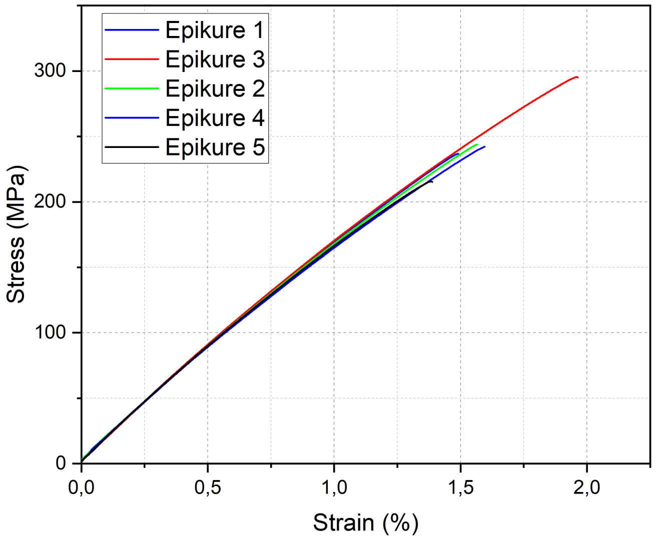


Figure 5.22: Scanning Electron Microscopy of the PHTE/Epikure04908 based laminate

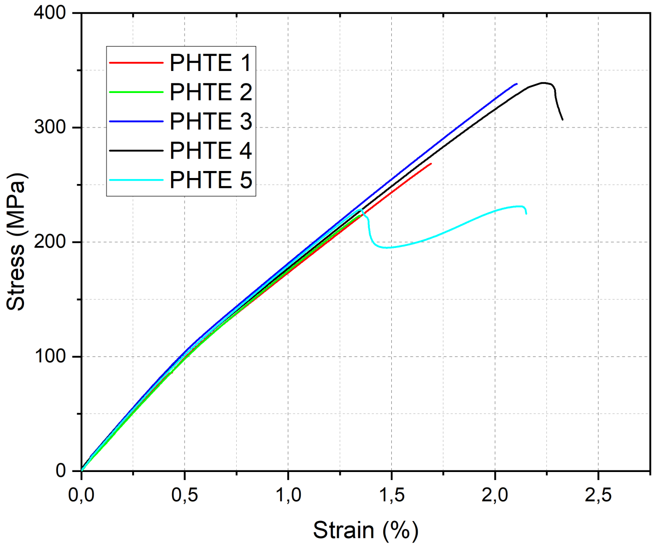
5.4. Composite Mechanical Testing

The mechanical properties of the composites were investigated in accordance with ASTM-D3039-08. Five samples for tensile testing of the resin were produced following the guidelines outlined in the standard (refer to Table 4.5). In the case of specimen 5 of PHTE, slipping occurred during the test, despite the presence of tabs on the specimen. This slipping is evident in the abrupt drop in stress observed in the stress-strain curve as shown in Figure 5.23. Consequently, the results from this specimen were not considered when determining the tensile strength.

The PHTE-based composite exhibited a tensile strength of 292 ± 57 MPa and a tensile modulus of 26 ± 2 GPa. In comparison, the tensile strength of the Epikote/Epikure04908-manufactured laminate was 247 ± 29 MPa, with a tensile modulus of 21 ± 1.7 GPa. The obtained mechanical properties as well as the normalized values are summarized in Table 5.11. These findings are further supported by the Stress-Strain curves of the two composites shown in Figure 5.23.



(a) Epikote/Epikure04908-based composite stress-strain



(b) PHTE/Epikure04908-based composite stress-strain

Figure 5.23: Stress-Strain curves obtained from the tensile test of the obtained composites

Table 5.11: Mechanical properties of PHTE and Epikote-based laminate obtained through Tensile Testing

	Strain (-)	**Tensile Strength (MPa)**	**Normalized Tensile Strength for 60% volume content (MPa)**	**Tensile Modulus (GPa)**	**Normalized Tensile Modulus for 60% volume content (GPa)**	**Maximum Force (kN)**
PHTE 1	0.01691	269	318	24	34	11.2
PHTE 2	0.01347	223	319	24	34	13.4
PHTE 3	0.02106	338	482	27	39	16.9
PHTE 4	0.02327	339	484	28	40	17.0
PHTE 5	0.02151	231	330	26	37	11.6
Average PHTE (MPa)	0.019244	292	387	26	37	14.6
Standard Deviation PHTE (MPa)	0.00398	57	79	2	2,5	
	Strain (-)	**Tensile Strength (MPa)**	**Normalized Tensile Strength for 60% volume content (MPa)**	**Tensile Modulus (GPa)**	**Normalized Tensile Modulus for 60% volume content (GPa)**	**Maximum Force (kN)**
Epikure 1	0.01491	237	323	22	33	11.80
Epikure 2	0.01566	244	333	21	32	12.20
Epikure 3	0.01964	295	402	23	35	14.70
Epikure 4	0.01596	242	330	19	29	12.10
Epikure 5	0.01388	216	295	21	32	10.80
Average Epikure (MPa)	0.01601	247	337	21	32	12.32
Standard Deviation Epikure (MPa)	0.00218	29	35	1.7	2	1.44

6

Conclusions

The primary aim of this thesis was to assess the feasibility of employing bio-based resins in composite manufacturing. This was accomplished by utilizing two approaches: firstly, by employing a commercially available bio-based epoxy derived from brown algae, and secondly, by attempting to synthesize an in-house bio-based benzoxazine resin. For the synthesis of the benzoxazine resins, a variety of precursors were employed, including m-guaiacol, furfurylamine, sesamol, paraformaldehyde, Jeffamine T403, and DDS. Additionally, a commercial bio-based epoxy, phloroglucinol triepoxy (PHTE), was utilized in the study.

The study encompassed a thorough material analysis and testing phase, which involved examining chemical properties and mechanical performance through various material characterization techniques. These techniques included FTIR (Fourier-transform infrared spectroscopy), TGA (thermogravimetric analysis), DSC (differential scanning calorimetry), DMA (dynamic mechanical analysis), and rheology analysis. Additionally, a range of mechanical tests were conducted as part of the study. Using the synthesized monomers and purchased epoxy, various simple composite structures were fabricated. These included square laminates with a $[0, 90, 0, 90]_s$ layup, which were produced to evaluate the quality of the potential composite products.

Six distinct bio-based benzoxazine monomers were successfully synthesized, with bio-content levels varying from 40 to 80%. While some minor issues and challenges were encountered during the synthesis process, it can be concluded that the fundamental chemistry required for producing bio-based benzoxazines is indeed feasible. However, despite successful synthesis, the curing behavior of these benzoxazines posed significant challenges. Less than half of the synthesized monomers demonstrated curing suitable for composite manufacturing, which is a critical step in determining the practical application of these resins. In addition to that, issues of brittleness and coloration were observed. The cured monomers displayed significant brittleness, with the samples easily disintegrating into a powdery form when gently squeezed between the fingers. Moreover, all of the samples acquired a deep black color after curing. This presents challenges, both from an aesthetic standpoint and practical considerations related to the inspection and visual assessment of the final composite material. These factors are of great significance, particularly in the context of commercial applications.

One notable positive finding, apart from the successful synthesis of the monomers, was the high thermal stability of the benzoxazine resins, especially for the sample based on sesamol and T043-Jeffamine. This quality is desirable in composites that are required to withstand high-temperature environments. Due to the extensive time and effort required to optimize the curing process for benzoxazines, and the uncertainty regarding the attainment of beneficial results for composite structures, the research focus was shifted towards exploring bio-based epoxies, specifically PHTE. However, while the initial results for bio-based benzoxazine resins in composite manufacturing were not entirely promising, their synthesis was an important step in understanding the potential and limitations of such materials. With further research and possibly the development of new curing agents or processes, the current obstacles might be overcome, potentially paving the way for their future use in sustainable composite materials.

PHTE stands out as a potential frontrunner in the quest for sustainable composite materials, mainly due to its impressive mechanical properties. These characteristics make PHTE an attractive candidate for a range of industrial applications. However, the material presents specific challenges in its practical implementation. One of the primary issues is its high viscosity and reactivity, which significantly complicates traditional manual manufacturing methods. This situation calls for a rethinking of manufacturing strategies, potentially shifting towards more technologically advanced or specialized techniques to harness the full potential of PHTE in composite manufacturing.

In-depth resin characterization of PHTE reveals an intriguing aspect of its physical properties - a high glass transition temperature (Tg). This property is especially noteworthy considering the resin's composition, which includes an aliphatic curing agent and a monofunctional reactive diluent, typically associated with a lower crosslinking density. Despite this, PHTE maintains a high Tg, suggesting its suitability for applications where thermal stability is critical. Moreover, the resin's formulation is partially bio-based, containing 60% bio-based carbon, aligning it with the growing emphasis on sustainability in material development. This eco-friendly aspect is a significant step towards meeting the increasing demand for environmentally responsible materials in various industrial sectors.

Adding to its thermal properties, PHTE exhibits high thermal stability, remaining stable up to temperatures as high as 320 °C. This attribute opens the door for its use in environments where materials are exposed to high temperatures, further broadening its application scope.

Despite these advantages, PHTE's mechanical behavior reveals a notable limitation – it displays increased stiffness in tension and flexural tests compared to the commercial BADGE system, but this is coupled with reduced strength. Even when the system was compared to the technical specifications of the Epikure/Epikote04908 system with factory specifications, without the addition of 10% diluent a significant increase in stiffness in both tensile and flexural properties was observed. This increase in stiffness came at the cost of a 24 % reduction in tensile strength and a 29 % reduction in flexural strength. However, once a more meaningful comparison was performed, by including diluent in the BADGE system samples an increase in both the stiffness and the strength was observed. It was apparent that the PHTE samples exhibited a clear brittle behavior. This brittleness, which is potentially linked to the reactive diluent in its formulation, poses a significant challenge.

Future research focusing on understanding and mitigating the impact of the reactive diluent could be key in enhancing PHTE's properties, making it a more robust and versatile option for sustainable composites. Addressing these challenges is crucial for leveraging PHTE's full potential in various industrial applications, especially in sectors where both environmental sustainability and material resilience are of paramount importance.

7

Recommendations and Future Work

The conclusions and results derived from this research indicate that the use of PHTE as a bio-based alternative to petroleum-based resins is very promising. This suggests that PHTE has the potential to play a significant role in the development of next-generation sustainable composite materials. However, further research and investigation is required for that to come in play. Future endeavors, derived and based on this study, could encompass several areas of research and development regarding PHTE formulation and its use in composite systems. These may include:

- **Expanding the Resin Characterization :** Expand further the characterization of the system PHTE/Epikure04908 so that the system could potentially utilised commercially.
- **Integration of Solid-State Inhibitors:** Incorporating solid-state inhibitors to extend the impregnation period, allowing for the use of vacuum infusion techniques to produce higher-quality composites.
- **Exploration of Hardener Systems :** Further investigation of PHTE in combination with hardeners similar to Epikure04908, particularly for use in high-speed Resin Transfer Molding (RTM) processes, where minimizing curing and processing times is crucial.
- **Utilization of Crystalline Hardeners:** Exploring the use of crystalline hardeners, such as 4,4 -Diaminodiphenyl sulfone (DDS), to target high-performance matrices, thus enhancing the composite's properties.
- **Exploration of Alternative Composite Manufacturing Techniques:** Researching alternative methods for composite manufacturing that may offer advantages in terms of performance, efficiency, and sustainability.
- **Proper Characterization of Mechanical Properties :** As previously indicated in the respective section, the mechanical test conducted did not yield valuable information concerning the mechanical properties of a PHTE-based composite. A more beneficial test, such as a cantilever beam test, could be employed to explore the adhesion of the resin to the fibers.
- **Distillation-Quality Functional Reactive Diluents:** Investigating the use of high-quality, functional reactive diluents to mimic industrial resin recipes for high-performance applications, ensuring consistent and reliable results.
- **Bio-based Fibers :** Consideration of the use of bio-based fibers, like flax, with a focus on secondary structures, particularly in aerospace applications, to create more environmentally friendly fiber-reinforced composites with high bio-content.
- **Possible Publication of the performed work :** The performed research regarding the PHTE system has been submitted to RSC Journal of Applied Polymers under the name ***”Algae-derived partially renewable epoxy resin formulation for glass fiber reinforced polymer composites”***.

Likewise, even though some initial results concerning the use of bio-based benzoxazine resins for composite manufacturing may not have been very promising, continued research and exploration in this area could pave the way for their potential utility and significance in the field. Several different studies can be made to lead to that :

- **Investigate Curing Method :** As per discussions with Professor Baris Kiskan from Istanbul Technical University (ITU), it is anticipated that brittleness and the observed color change during the curing process of benzoxazine monomers may occur. In certain instances, Professor Kiskan's team successfully addressed this challenge by employing a step-curing approach for the synthesized monomers. In this method, the benzoxazines are subjected to thermal curing, beginning at 100°C and progressing in 20°C increments up to 180°C, with each temperature step being maintained for a duration of 1 hour.
- **Investigate the use of Benzoxazines for other applications :** While the application of the synthesized bio-based benzoxazines may have presented challenges in the context of this particular research, it became evident that the obtained monomers held the potential for other uses. During the curing of certain monomers, it was noticeable that the cured samples exhibited strong adhesion to the small aluminum plates on which they were positioned. Their high thermal stability, flame retardancy, and promising adhesion properties suggest that the synthesized monomers could find utility in alternative applications, such as functional coatings for various purposes.
- **Investigate the effect of functional groups :** During the sythesis steps of the bio-based benzoxazines several issues appeared. Some of those, namely the reactivity of the systems, could be associated with the functional groups present in the precursors and the benzoxazine monomers. Investigating the effect of the functional groups is crucial, as they can significantly influence the reactivity and cross-linking density of benzoxazines. Further studies should focus on how different substituents (e.g., alkyl, aryl, alkoxy), but also the location on the benzene ring, affect these properties. This could involve synthesizing a range of benzoxazine monomers with varying functional groups and analyzing their curing behavior and the properties of the resulting polymers.

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A

Chemical Reactions and Pre-Cursors for Benzoxazine Synthesis

In this appendix, the obtained monomers, along with the precise weights and equivalent weights of the precursor materials used, are presented. The chemical structure of each monomer is followed by a table containing the exact weights utilized. Additionally, a brief description of the synthesis steps is provided:

BG1 - Monofunctional Guaiacol

Sample BG1 was based on M-guaiacol, Furfurylamine, and Formaldehyde :

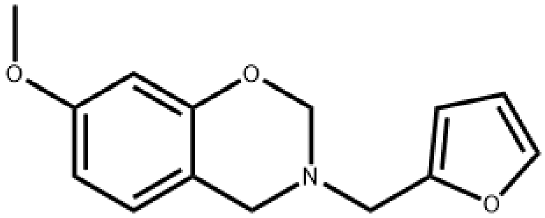


Figure A.1: BG1 : M-Guaiacol/Fu monomer

The exact synthesis followed for this monomer is described in the main body of the research report.

BG2 - Bis-functional Guaiacol

Sample BG2 was based on M-guaiacol, 4,4-DDS and Formaldehyde :

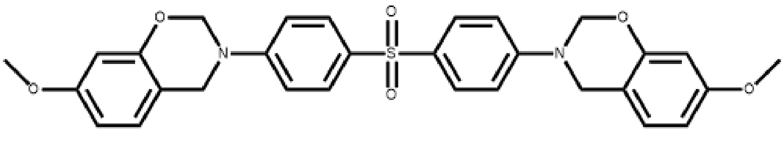


Figure A.2: BG2 : M-Guaiacol/4,4 DDS

Pre-cursors Used	Molar Mass	Actual Mass (g)	Equivalent Weights
M-Guaiacol	124,14	37.24	2
4,4-DDS	248.3	37.3	1
Paraformaldehyde	30	18	4

1. Dissolve M-guaiacol + DDS in Dioxane (500 mL in RBF)
2. Stir for 1-2 hours
3. Add P-formaldehyle and heat to 110 °C for 6 hours
4. Rotary Evaporate Dioxane
5. Dissolve in DCM
6. Wash with 1 M NAOH ($\approx 500ml$) and three times with DI
7. Dry over $MgS0_4$ and filter
8. Rotary evaporate DCM
9. Dry in oven at 60 ◦C for 2 hours

BG3 - Tri-functional Guaiacol

Sample BG1 was based on M-guaiacol, T403-Jeffamine and P-Formaldehyde :

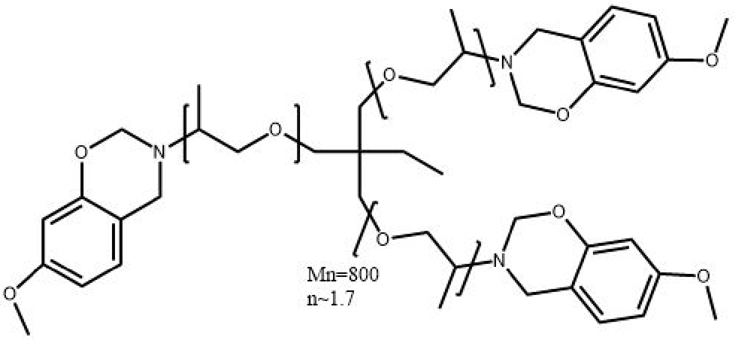


Figure A.3: BG2 : M-Guaiacol/4,4 DDS

Pre-cursors Used	Molar Mass	Actual Mass (g)	Equivalent Weights
M-Guaiacol	124.4	40.3	3
T-403	440	47	1
Paraformaldehyde	30	26.5	6

1. Dissolve M-guaiacol + T403-Jeffamine in Dioxane (500 mL in RBF)
2. Stir for 10 minutes
3. Add P-formaldehyde and heat to 110 °C for 5 hours
4. Rotary Evaporate Dioxane
5. Dissolve in DCM ($\approx 200ml$)
6. Wash with 1 M NaOH ($\approx 500ml$) : **emulsion was formed in the NaOH solution**
7. Wash three times with DI ($\approx 500ml$)
8. Dry over $MgS0_4$ and filter
9. Rotary evaporate to remove DCM

BS1 - Mono-functional Sesamol

Sample BS1 was based on Sesamol, Furfurylamine and P-Formaldehyde :

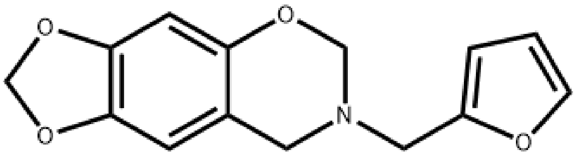


Figure A.4: BS1 : Sesamol/Furfurylamine

Pre-cursors Used	Molar Mass	Actual Mass (g)	Equivalent Weights
Sesamol	138.12	52.3	1
Furfurylamine	99.12	36.1	1
Paraformaldehyde	30	26.1	2

1. Dissolve Sesamol + Furfurylamine in Dioxane (500 mL in RBF)
2. Stir for 10 minutes
3. Add P-formaldehyde and heat to 110 °C for 6 hours
4. Rotary Evaporate Dioxane
5. Dissolve in DCM : **Sample did not dissolve in DCM- removed and dried**
6. Wash with 1 M NaOH ($\approx 500ml$) and three times with DI
7. Dry over $MgS0_4$ and filter

BS2 - Bis-functional Sesamol

Sample BS2 was based on Sesamol, 4,4-DDS and P-Formaldehyde :

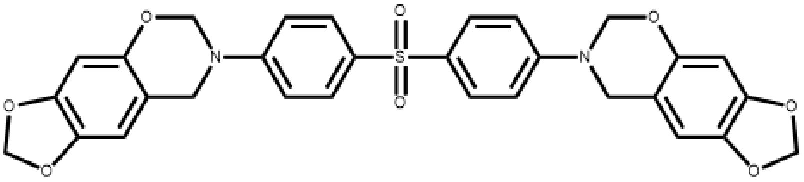


Figure A.5: BS2 : Sesamol/4,4 DDS

Pre-cursors Used	Molar Mass	Actual Mass (g)	Equivalent Weights
Sesamol	138.12	41.4	2
4,4-DDS	248.3	38	1
Paraformaldehyde	30	18.6	4

1. Dissolve Sesamol + DDS in Dioxane (500 mL in RBF)
2. Stir for 10 minutes
3. Add P-formaldehyde and heat to 110 °C for 8 hours : **Initially all reagents dissolve at 100 °C. After the 8 hours solution was thick with precipitate**
4. Rotary Evaporate Dioxane
5. Filter using a Buchner funnel
6. Wash with 1 M NaOH ($\approx 500ml$) and three times with DI ($\approx 500ml$

7. Dry over $MgS0_4$ and filter
8. Dry in a vacuum oven at 60 °C for 2 hours

BS3 - Tri-functional Sesamol

Sample BS3 was based on Sesamol, T403-Jeffamin and P-Formaldehyde :

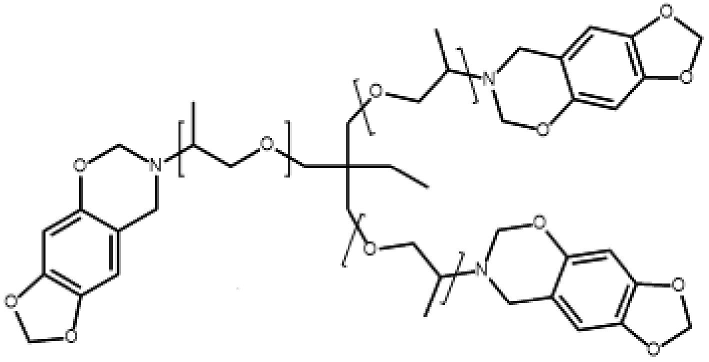


Figure A.6: BS3 : Sesamol/T403 Jeffamine

Pre-cursors Used	Molar Mass	Actual Mass (g)	Equivalent Weights
Sesamol	138.12	42	3
T-403	440	44	1
Paraformaldehyde	30	22	6

1. Dissolve Sesamol + T403-Jeffamine in Dioxane (500 mL in RBF)
2. Stir for 10 minutes
3. Add P-formaldehyde and heat to 110 °C for 16.5 hours
4. Rotary Evaporate Dioxane
5. Dissolve in DCM ($\approx 200ml$)
6. Wash with 1 M NaOH ($\approx 500ml$) and three times with DI ($\approx 500ml$)
7. Dry over $MgS0_4$ and filter
8. Rotary evaporate to remove DCM

B

Ring Opening Mechanisms

In this appendix, the ROP (Ring Opening Mechanism) will be explained in a bit more detail.

The detailed mechanism of Ring-Opening Polymerization (ROP) of benzoxazines is a complex chemical process as described in section 2.1, but it can be described in a more detailed manner, focusing on the key steps and the molecular changes involved. This process is pivotal in creating polybenzoxazines

- **Benzoxazine Monomer Formation:** Benzoxazines are synthesized through a Mannich condensation reaction between phenols, formaldehyde, and primary amines leading to the creation of a benzoxazine monomer, containing a benzene and an oxazine ring – a cyclic structure comprising nitrogen, oxygen, and carbon atoms.
- **Activation and Ring-Opening:** The ROP begins thermally activating of the monomer. By increasing the temperature up to a specific threshold the ROP begins. The oxazine ring is strained and becomes thermolabile. The ring undergoes cleavage, between oxygen and carbon in the ring, leading to an activated, open-chain structure. Reactive sites are formed, necessary for polymerization.
- **Polymerization Mechanism :** The monomer has active sites; the reactive carbon which was part of the oxazine ring and the nitrogen atom. Nucleophilic attacks between different monomers take place. A new covalent bond is formed between the carbon atom of one monomer and the nitrogen atom of another. This leads to the formation of a linear polymer chain through a step-growth mechanism. The reaction continues, adding more monomers to the growing chain.
- **Formation of Three-Dimensional Network and Crosslinking :** As the polymerization progresses, the linear chains start to crosslink with each other. This is helped by the multifunctionality of the benzoxazine monomers (having multiple reactive sites). The cross-linking process results in the transformation from a linear or branched polymer structure to a rigid, three-dimensional network.

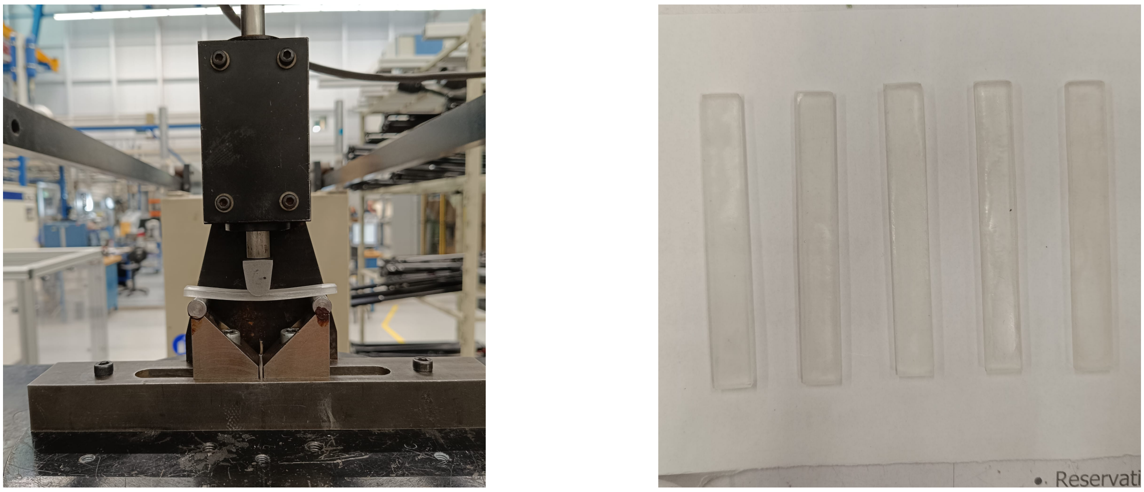
C

Dimensions and Data for Epikote/Epikure04908 system mechanical tests

In this appendix, the exact dimensions, and remarks regarding the samples used for tensile and flexural testing using Epikote/Epikure04908 system including 10% diluent are given in the following tables:

Table C.1: Sample dimensions of Epikote/Epikure04908 flexural specimen

Sample	**L (mm)**	**w (mm)**	**t (mm)**	**Remarks**
FR1	79.86	9.91	4.11	Needed grinding to make, surfaces parallel and flush
FR2	79.82	9.90	4.21	No obvious remarks worth mentioning
FR3	79.67	10.01	4.21	Small piece was chipped off at one of the sides
FR4	80.08	9.86	3.93	Concave shape on one side of the sample. Optical observation verified by thickness measurements
FR5	79.72	9.84	4.13	No obvious remarks worth mentioning. Good quality sample



(a) Flexural testing of Epikote system

(b) Specimen for flexural testing of Epikote system

Figure C.1: Flexural Test Epikote/Epikure System with 10% diluent

Table C.2: Sample dimensions of Epikote/Epikure04908 Tensile specimen

Sample	L (mm)	w1 (mm)	w (mm)	t (mm)	Remarks
TR1e	130.12	6.11	18.88	3.91	*Good Specimen*
TR2e	129.5	6.09	19.91	4.03	*Bit chipped off at the top grip location*
TR3e	129.20	6.11	18.84	3.93	*Shrinkage observed in one of the sides from curing*
TR4e	129.03	6.13	19.27	3.86	*No obvious remarks worth mentioning*
TR5e	129.45	6.09	18.93	3.86	*Concave shape on one side*


(a) Tensile test set-up of Epikote/Epikure system

(b) Specimen for tensile testing of Epikote system

(c) Failed Specimen for flexural testing of Epikote system

Figure C.2: Tensile Test Epikote/Epikure System with 10% diluent