

National University of Science and Technology Politehnica Bucharest

Doctoral School of Chemical Engineering and Biotechnologies

Ph.D. Thesis Summary

Design and synthesis of bio-sourced benzoxazine based materials from natural phenols: toward environmentally friendly and application-oriented composites and hybrid systems

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1. Conceptual framework and core problem statement

The increasing demand for sustainable yet high-performance materials has driven research into renewable alternatives to petroleum-based thermosetting polymers.

This thesis explores the design and synthesis of novel bio-based benzoxazine monomers as sustainable alternatives to conventional petroleum-derived thermosetting resins. By employing renewable feedstocks and rational molecular design, structurally diverse benzoxazines were prepared and characterized, demonstrating excellent thermal and mechanical properties. In addition to the development of these monomers, the research also focused on translating molecular innovation into application-oriented materials. Nanocomposites based on the newly synthesized benzoxazines were fabricated for target-specific uses, including electromagnetic interference shielding, while hybrid networks were created by combining bio-sourced benzoxazines with epoxidized linseed oil and thiols. These hybrid systems exploited synergistic interactions between bio-based and synthetic components, yielding tunable performance characteristics and enhanced processing flexibility.

The work highlights not only the scientific novelty of creating high-performance polymers from renewable resources, but also their industrial relevance. The bio-based benzoxazines and their composites offer compatibility with existing manufacturing processes, which reduces barriers to implementation. They align with increasing regulatory and societal demands for sustainable materials, while maintaining the thermal stability, mechanical strength, and multifunctionality required in advanced sectors such as aerospace, automotive, electronics, and construction. Moreover, by valorizing renewable feedstocks, the approach has potential economic advantages and contributes to reducing dependence on petroleum-derived chemicals. Taken together, this research demonstrates that bio-based benzoxazines are not only academically promising but also strategically important for industries seeking to reconcile high performance with environmental responsibility.

2. Literature overview and scientific context

Polybenzoxazine resins represent a modern class of phenolic thermosets synthesized by polymerization of benzoxazine-type monomers. These resins benefit of a thriving interest as they combine and surpass the advantages of both classical epoxy and phenolic resins. Owing to their outstanding thermal, chemical, and mechanical properties polybenzoxazine have played a leading role in the development of cutting-edge technologies that supported the development of valuable industries such as aerospace, coatings, ballistic and microelectronics [1-3].

Benzoxazine monomers can be synthesized by facile Mannich condensation, a three-component chemical reaction that involves phenol, primary amine and formaldehyde. Depending on the functionality of the reactants involved in the synthesis, different types of monomers can be obtained. There are four main categories namely [4, 5]:

(i) First generation benzoxazine

(ii) Second generation benzoxazine.

(iii) Third generation benzoxazine

(iv) Fourth generation benzoxazines

Polybenzoxazines represent a new generation of thermosetting materials that successfully overcome many of the inherent shortcomings associated with conventional systems such as resoles, novolacs, and epoxies. Traditional thermosets often suffer from limited mechanical performance, require catalysts to initiate curing reactions, and may release unwanted by-products during thermal treatment. In contrast, polybenzoxazines bypass these drawbacks through their unique molecular configuration and auto catalytic curing mechanisms [6].

One of the most remarkable features of polybenzoxazines is their near-zero curing shrinkage upon polymerization, which ensures dimensional stability and minimizes residual stresses, an important advantage in precision applications. In addition, these materials demonstrate excellent chemical resistance, high glass transition temperatures (T_g), superior thermal stability, and elevated char yields, making them particularly resilient under demanding operating conditions. Their low surface energy and minimal water absorption further enhance performance, ensuring long-term durability even in harsh environments. Notably, the curing reaction of polybenzoxazines

typically proceeds without the need for external catalysts and generates no by-products, simplifying processing while improving both environmental and operational safety [3, 6].

These distinctive characteristics make polybenzoxazine resins highly versatile and adaptable. They are increasingly recognized as advanced materials capable of meeting the stringent requirements of a broad range of industries. Applications extend from automotive and aerospace where lightweight, high-strength, and heat-resistant components are essential to coatings and adhesives that demand durability and chemical resistance, as well as electronics, where thermal stability and low moisture uptake are critical [7-9]. As such, polybenzoxazines are emerging as a key enabler for next-generation high-performance materials in both structural and functional domains.

2.1. Bio-based benzoxazine

Driven by the demand for environmentally friendly and sustainable materials, bio-based benzoxazines have emerged as a promising class of monomers, as was also noted from the previous discussions. The increasing demand for high-performance materials along with the growing awareness toward the environment preservation has created a strong impetus to develop inexpensive, sustainable alternatives for conventional polymers by employing natural resources instead of conventional petroleum-based chemicals.

Over the last decade the design of benzoxazine thermosets became more oriented towards green chemistry and thus biomass resources replacing the conventional phenol, primary amine and formaldehyde were involved in the *Mannich* condensation reaction. Nowadays, the substitution of petroleum precursors by considering natural alternatives have unlocked alternatives to design green or at least bio-based materials that are capable to outreach the performances of conventional benzoxazines. The versatility of these polymeric materials represents one of the central assets around which desirable properties can be tailored. Up to now, bio-based compounds such as vanillin [10], guaiacol [11], eugenol [12], resorcinol [13], furfurylamine [14], salicylaldehyde [15] and lignin [16] were successfully used in the synthesis of advanced polybenzoxazine networks that showed their potential as promising alternatives to the conventional petroleum-based thermosets [17].

Superior thermal and mechanical properties, combined with the ability to tailor surface and electrical characteristics while adhering to the principles of green chemistry, represent the most

significant advances achieved through the development of novel benzoxazine monomers reported in the past two years [18-20]. These innovations highlight how molecular design strategies are increasingly focused not only on performance but also on sustainability, creating a new generation of high-value thermosetting systems.

Despite these advantages, polybenzoxazine coatings are often hindered by a fundamental drawback: brittleness. This limitation has driven researchers to prioritize the development of more flexible benzoxazine-based systems. One promising strategy lies in the creation of benzoxazine–epoxy copolymers, which have recently attracted considerable attention, particularly in formulations derived from bio-sourced monomers. By integrating renewable feedstocks, these systems align with environmental objectives while simultaneously broadening their functional scope. In particular, the incorporation of epoxidized vegetable oils (such as linseed oil and castor oil) has been shown to not only enhance flexibility but also impart advanced functionalities, including shape memory effects and self-healing capabilities [21-23]. Such multifunctional materials are especially valuable in high-performance coatings, smart adhesives, and protective films, where durability and adaptability are equally important.

Another powerful strategy to overcome brittleness and improve mechanical versatility involves the incorporation of urethane units into benzoxazine copolymeric networks. This approach leverages the complementary strengths of both components: benzoxazine resins provide exceptional thermal and mechanical stability, while polyurethanes contribute adhesion, toughness, and flexibility. Importantly, the chemical structures of both monomers are rich in functional groups capable of forming multiple hydrogen bonds. These supramolecular interactions serve as a molecular reinforcement mechanism, endowing the resulting copolymers with a unique balance of rigidity and elasticity, along with enhanced resistance to environmental degradation [24-26].

Taken together, these recent advances demonstrate how strategic molecular engineering, whether through bio-based feedstocks, epoxy co-networking, or urethane incorporation can significantly expand the property spectrum of benzoxazine systems. The resulting materials not only address traditional limitations such as brittleness but also open pathways toward smart, multifunctional coatings and resins tailored for emerging industrial applications. In this context, the synergy between performance optimization and sustainable design positions benzoxazine-based polymers as a promising platform for the next generation of advanced thermosetting materials.

2.2. Composite materials based on benzoxazine

Benzoxazine composites represent a valuable class of materials with applications in advanced industries where durability, high thermal stability and flame resistance are essential requirements [27, 28]. There are four main types of composite formulations, based on the following reinforcing agents:

- (i)** carbon-based nanostructures
- (ii)** clays
- (iii)** fiber
- (iv)** inorganic particles

Each of these reinforcements imparts unique advantages. Carbon-based nanostructures, including graphene derivatives, carbon nanotubes, and carbon fibers, offer superior mechanical reinforcement and electrical conductivity, making them attractive for aerospace and electronic shielding applications. Clays provide improved barrier properties and enhanced flame retardancy, while inorganic fillers such as silica or metal oxides improve dimensional stability and thermal performance. Fiber reinforcements ranging from high-performance glass or aramid fibers to natural bio-fibers significantly contribute to mechanical strength and toughness, thereby broadening the application scope of benzoxazine composites.

2.3. Bio-based benzoxazine composites

In recent years, a growing body of research has focused on integrating sustainability into composite design, leading to the emergence of bio-based benzoxazine composites. Traditionally, the discussion around "bio-based" materials in this field has centered on the renewable origin of the benzoxazine monomer itself. However, a broader and equally important perspective considers reinforcing agents, which may also be derived from natural resources.

Natural fibers such as hemp, flax, jute, and sisal have been successfully incorporated into benzoxazine matrices to yield lightweight, renewable composites [29-31]. These fibers not only provide mechanical reinforcement but also contribute to reducing the overall environmental footprint of the final materials. Furthermore, the chemical compatibility between hydroxyl-rich natural fibers and the benzoxazine matrix often facilitates favorable interfacial interactions, improving adhesion and mechanical integrity.

Beyond fibers, other natural reinforcements such as lignin-derived nanoparticles, cellulose nanocrystals, and biochar are beginning to attract attention for their ability to combine sustainability with advanced functionality. For example, cellulose nanocrystals can enhance stiffness and barrier properties, while lignin-based fillers may contribute to flame retardancy. The integration of such renewable reinforcements complements the inherent green chemistry principles of benzoxazine resins, thus paving the way for fully sustainable high-performance composites.

The coupling of benzoxazine chemistry with advanced or bio-based reinforcements has unlocked a wide spectrum of multifunctional composites. On the one hand, high-tech reinforcements like graphene oxide or carbon fibers endow these systems with state-of-the-art performance for aerospace, automotive, and electronic applications. On the other hand, renewable fibers and natural nanostructures establish a route toward sustainable, eco-efficient composites, without compromising mechanical strength or thermal stability.

Looking forward, future research is likely to focus on hybrid strategies that combine both synthetic high-performance and natural reinforcements within benzoxazine matrices. Such approaches could yield materials that simultaneously satisfy industrial performance requirements while meeting circular economy and environmental sustainability goals. This convergence of functionality, processability, and eco-conscious design positions benzoxazine-based composites as one of the most promising platforms for the next generation of advanced structural and functional materials.

3. General and specific objectives of the research

The main goal of the research plan was to develop viable formulations with complex molecular architecture with configurable properties.

The **general objective** of the current thesis stands in the *design, synthesis and thorough characterization of bio-based benzoxazine monomers and their composites and hybrids along with their assessment as potential substitutes for the conventional petroleum-based thermosets*. In order to accomplish this goal, the present research was divided into **two main objectives** with specific activities that have been defined along with the corresponding methodologies.

Within this framework, the *first direction* of the thesis was to design, synthesize and characterize bio-benzoxazines based on polyethyleneimine and natural phenols (sesamol, vanillin

and eugenol) and to evaluate the benefits brought by their different chemical structures to the final performances.

The *second research direction* focused on the development of new composites and hybrid networks by exploring the versatility of polyethyleneimine bio-based benzoxazines with free amino groups, with special emphasis on the design of formulations with applicability in different advanced industries. The main goal was to evaluate the ability of benzoxazine complex monomers to chemically interact with graphene oxide and carbon fibers, aiming to generate an advanced lightweight composite system as a strong candidate for electromagnetic interference shielding material.

As a co-extension, but embodied as a *third direction*, the use of the biobased benzoxazine monomer of polyethyleneimine as a generator of the amine component for epoxidized linseed oil and thiols as the second network, for the development of innovative hybrids, was investigated. The influence of thiol type and concentration on thermal, mechanical and nanomechanical properties has been studied by means of different advanced techniques.

4. Original contributions

The **first article** “*Insightful characterization of sesamol-based polybenzoxazines: Effect of phenol and amine chain type on physical and nanomechanical properties*” presents a systematic study on the influence of molecular structure on the performance of bio-based polybenzoxazines. Sesamol, a naturally occurring phenolic compound, was employed as the core renewable building block for the synthesis of a series of benzoxazine monomers with varying amine chain lengths. The resulting polymers were subjected to detailed spectroscopic, thermal, morphological, and nanomechanical analyses to establish comprehensive structure–property relationships.

The results demonstrate that the chain length of the amine has a pronounced effect on polymerization behavior, crosslinking density, thermal stability, and glass transition temperature. Furthermore, nanoscale mechanical studies revealed that the rigidity, hardness, and modulus of the polybenzoxazines were strongly dependent on the length of the aliphatic amino substituent. Rigid and aromatic chain structures contributed to enhanced thermal and mechanical properties, while more flexible aliphatic substituents imparted tunability in toughness and processability.

By correlating molecular design parameters with bulk and nanoscale material performance, the study provides valuable insights into how sesamol-derived benzoxazines can be rationally tailored for advanced applications. The findings underscore the potential of bio-based benzoxazines as sustainable alternatives to petroleum-derived resins, with performance levels suitable for high-end industrial sectors.

The **second article** “*Synthesis and thermo-mechanical characterization of vanillin-based polybenzoxazines with complex architecture*” reports the preparation of bio-based benzoxazine monomers using natural phenols, namely vanillin and eugenol, in reaction with paraformaldehyde and branched polyethyleneimine (PEI). The incorporation of these renewable phenolic resources aims to expand the library of sustainable thermosetting polymers while simultaneously addressing limitations such as high curing temperatures and brittleness observed in conventional benzoxazines.

Structural characterization by FT-IR, ¹H-NMR, and GPC confirmed the successful grafting of oxazine rings along the PEI backbone, though steric hindrance effects limited the conversion of primary amine groups into oxazine structures. Differential scanning calorimetry revealed relatively low curing temperatures (166–218 °C), with eugenol-derived monomers polymerizing at lower temperatures than their vanillin-based counterparts, likely due to the reactive allyl group. Thermogravimetric analysis demonstrated multi-step degradation with substantial char yields (~32%), corresponding to limiting oxygen index values near 30, indicating intrinsic flame-retardant behavior.

Mechanical evaluation through nanoindentation showed distinct differences between the two systems: eugenol-based polybenzoxazines displayed higher hardness and stiffness, attributed to the allyl group’s involvement in crosslinking, while vanillin-based analogues exhibited lower nanomechanical performance but improved surface characteristics. Contact angle measurements confirmed that both resins are hydrophilic due to the polar functionalities of PEI, with vanillin-based systems displaying a slight shift toward hydrophobicity as a result of hydrogen bonding from formyl groups.

Overall, the study demonstrates that natural phenols such as vanillin and eugenol can be employed to design polybenzoxazines with tunable thermal, mechanical, and surface properties. The high char yields, fire resistance, and improved processability position these bio-based thermosets as promising candidates for advanced industrial applications where sustainability and performance must be reconciled.

The **third article** “*A ternary multiscale nanocomposite system based on functionalized graphene oxide, carbon fibers and bio-based polybenzoxazine for electromagnetic shielding*” presents a ternary multiscale nanocomposite for electromagnetic shielding built on a bio-based polybenzoxazine (SP-PBz) matrix reinforced with carbon fibers (CF) and tetraethylene-pentaamine–functionalized reduced graphene oxide (GT).

This study demonstrates that ternary nanocomposites based on bio-based polybenzoxazine, carbon fibers, and functionalized reduced graphene oxide (GT) can successfully combine sustainability with high performance. The incorporation of GT into the polybenzoxazine matrix was shown to have a catalytic effect on the curing process, lowering the polymerization temperature and activation energy, which facilitates more efficient crosslinking. The addition of carbon fibers greatly improved thermal stability and char yield, leading to materials with strong flame-retardant properties.

From a mechanical perspective, the nanocomposites displayed significant reinforcement compared to the neat polybenzoxazine, with carbon fibers increasing stiffness by more than two orders of magnitude. The optimal performance was achieved at a GT loading of 2 wt.%, where the materials exhibited the highest modulus and hardness, supported by uniform dispersion and strong interfacial adhesion through hydrogen bonding, π – π stacking, and covalent interactions. At higher GT contents, agglomeration effects diminished local mechanical performance.

Electromagnetic shielding tests confirmed that these composites are highly effective in the X-band frequency range (8–12 GHz), with shielding efficiency dominated by absorption mechanisms. The effectiveness increased with GT content, peaking above 18 dB at 3 wt.% loading, where conductivity values reached up to 40 S/m.

Overall, the findings indicate that a 2 wt.% GT content provides the best balance of thermal stability, mechanical reinforcement, and interfacial compatibility, while 3 wt.% GT maximizes electromagnetic shielding performance. These results highlight the potential of bio-based benzoxazine systems, when combined with carbon fibers and graphene derivatives, to serve as lightweight, thermally robust, and multifunctional materials for advanced industrial applications.

The **fourth article** “*Multi-functional hybrid terpolymer thermosets based on thiols bio-based epoxy and benzoxazine monomers*” reports the design of hybrid terpolymer thermosets built from an eugenol-based polybenzoxazine oligomer (EPB), epoxidized linseed oil (ELO), and thiol

crosslinkers of different functionality (di-thiol 2SH and tri-thiol 3SH). Curing pathways and kinetics were elucidated by FTIR and DSC.

The study shows that eugenol-based polybenzoxazine (EPB) can be compatibilized with epoxidized linseed oil (ELO) and thiol crosslinkers to create hybrid, bio-based terpolymer networks whose properties are predictably tunable through thiol functionality and loading. FTIR/DSC evidence a multi-path curing scheme—benzoxazine and epoxy ring-openings coupled with thiol-epoxy and thiol-ene reactions, catalyzed by amines and phenolic OH that shifts to lower temperatures and lower apparent activation energies as thiol content increases. This compositional control translates directly into network architecture: low thiol levels (~0.25 wt.%) maximize stiffness and crosslink density (compact meshes, single $\tan \delta$ peak indicative of good miscibility), whereas higher levels (0.5–1 wt.%) drive more elastomeric behavior with reduced T_g due to flexible thio/ether linkages and greater chain mobility. Tri-functional thiol (3SH) tends to build denser, more uniform networks than di-thiol (2SH), while 2SH can behave more like a chain extender.

Thermally, all formulations retain robust stability ($T_d 5\% \sim 290\text{--}310^\circ\text{C}$), and thiol-modified systems show increased residual mass and $\text{LOI} > 22$, supporting flame-resistant coating applications. Nanoindentation mirrors the DMA trends, with peak surface stiffness around 0.25 wt.% 3SH and highest ductility at 1 wt.% 2SH. Surfaces become progressively more hydrophobic as thiol content rises (water contact angles $\sim 104^\circ$ at 1 wt.%), consistent with tighter hydrogen-bonded networks; however, alkaline media favor ester hydrolysis (β -hydroxy/thioesters), accelerating degradation, while acidic conditions increase uptake via protonation of sulfur-containing groups. High gel fractions ($\sim 95\text{--}100\%$) confirm efficient network formation.

In short, the work establishes a composition-driven design map: use ~0.25 wt.% thiol (preferably 3SH) when high stiffness and crosslink density are needed at moderate T_g and increase thiol to 0.5–1 wt.% when flexibility and lower T_g are desired—without sacrificing baseline thermal stability or flame resistance intrinsic to the EPB/ELO platform.

To sum up, the present thesis has explored the design, synthesis, and application of novel **bio-based benzoxazine monomers and their hybrid materials and nanocomposites**, with the overarching goal of demonstrating that sustainable thermosetting polymers can meet or even exceed the performance of conventional petroleum-derived systems. By employing renewable phenolic resources such as sesamol and eugenol, alongside epoxidized linseed oil and thiol

crosslinkers, a versatile platform of materials was developed with tunable curing behavior, network architecture, and multifunctional properties.

A first line of investigation focused on **fundamental structure–property relationships**, where the nature of the phenolic and amine components was shown to directly dictate the thermal, mechanical, and nanomechanical performance of sesamol-based polybenzoxazines. These insights provided a clear basis for tailoring molecular design to balance stiffness, toughness, and processability. Building on this, the incorporation of epoxidized oils and thiols enabled the formation of **hybrid terpolymer networks** with adjustable crosslink density and glass transition temperatures. By controlling thiol type and loading, it was possible to shift materials from rigid, highly crosslinked coatings to more flexible, elastomeric systems, while preserving flame resistance and thermal stability.

A second line of work extended bio-based benzoxazine systems toward **multifunctional nanocomposites**. Through the integration of carbon fibers and functionalized reduced graphene oxide, ternary composites were engineered with synergistic reinforcement across length scales. At optimal loading levels, significant increases in stiffness, modulus, and hardness were achieved, while electromagnetic shielding effectiveness in the X-band exceeded 18 dB. These results demonstrate not only the capacity of bio-derived thermosets to achieve structural performance comparable to advanced engineering resins, but also their ability to deliver **functional properties such as EMI attenuation**.

Taken together, the results of this thesis provide a **comprehensive framework for the development of next-generation bio-based thermosetting polymers**. The combined strategies of molecular design, hybrid network formation, and nanocomposite engineering show that mechanical, thermal, and functional performances can be systematically tuned through composition and processing. Importantly, all systems retained excellent flame resistance, thermal stability, and structural integrity, confirming their potential relevance to industrial applications in aerospace, automotive, electronics, and protective coatings.

5. General conclusion

For the very first time, it was shown that the intrinsic chemical architecture of renewable phenolic sources and amines decisively governs oxazine ring formation, thereby shaping the thermal and mechanical performance of bio-based benzoxazines.

In addition, amino-functional bio-benzoxazines were developed using branched polyethyleneimine, whose abundant free amino groups enabled multiple interactions. This breakthrough establishes a new foundation for designing versatile thermosetting resins and hybrid polymer networks.

Sesamol was validated as a renewable and sustainable candidate for benzoxazine monomers delivering high performance while remaining firmly aligned with environmental sustainability goals.

Bio-benzoxazine nanocomposites, reinforced with functionalized graphene oxide and carbon fibers, were established as cutting-edge EMI shielding materials. These high-performance systems pave the way for next-generation applications in electronics and aerospace.

Functionalized graphene oxide was shown to reduce polymerization temperature, thereby improving processing efficiency. At the same time, thiol crosslinkers provide fine control over mechanical strength and hydrophobicity features that make these materials highly attractive for industrial scale-up.

Together, this body of work introduces a materials toolbox of renewable, multifunctional, and readily processable benzoxazine systems, holding clear promise for sustainable composites, high-performance coatings, and advanced electronic devices.

In conclusion, this work demonstrates that **bio-based benzoxazine chemistry is not only a sustainable alternative to petroleum-based resins, but also a pathway to multifunctional materials with broad application potential**. By bridging renewable chemistry with advanced materials design, this thesis contributes both to the scientific understanding of bio-derived thermosets and to the practical advancement of greener, high-performance polymer systems.

6. List of publications included in the thesis

1. **Necolau M.I.**, Biru E.I., Ghitman J., Stavarache C., Iovu H., (2022). "Insightful characterization of sesamol-based polybenzoxazines: Effect of phenol and amine chain type on physical and nanomechanical properties", **Polymer Testing**, 110, 107578, **Q1, IF 6**
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