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ORIGINAL PAPER

Investigation of the structural features and polymerization mechanism of a novel bio-based benzoxazine using different lewis acids

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Abstract
Benzoxazines are heterocyclic compounds known for their high thermal stability, flame retardancy, and excellent mechanical performance, making them promising candidates for high-performance polymer applications. This study aimed to synthesize a benzoxazine monomer (Ca-c) derived from cardanol (Ca), the main component of cashew nut shell liquid (CNSL), using hexamethylenetetramine (HMTA) as a source of both methylene and nitrogen units, and to evaluate the influence of Lewis acids ($AlCl_3$, $FeCl_3$, $MgCl_2$, and $ZnCl_2$) on the polymerization process. The monomer was synthesized from cardanol and HMTA, producing a resin that was employed without further purification. Formulations were prepared by incorporating metal salts at 7.5% (mol/mol), followed by curing under a controlled heating protocol. This approach enabled evaluation of the influence of the salts on the curing behavior and properties of the benzoxazine system. Characterization by FTIR and NMR (^1H and ^{13}C) confirmed the formation of the oxazine ring. DSC analyses revealed a significant reduction in the onset polymerization temperature, especially with $MgCl_2$ (up to 29 °C). TGA showed good thermal stability, and diffuse reflectance spectroscopy indicated metal–ligand interactions, particularly in the Zn^{2+}-containing systems. The results demonstrate that metal salts act as effective catalysts, enabling efficient polymerization under milder conditions.

Keywords Cardanol · Thermal analysis · Bio-based monomer · Lewis acid catalysis

Introduction

Benzoxazines are a class of heterocyclic compounds known for their remarkable properties, including high thermal stability, flame retardancy, low water absorption, and good mechanical strength. These characteristics make them excellent candidates for various applications, especially as monomers in the synthesis of advanced polymers [1–7].

Over the past decades, benzoxazines have attracted increasing attention as high-performance thermosetting resins due to their exceptional physical and chemical properties. During this period, polybenzoxazines have evolved from conventional petroleum-based systems to more advanced generations specifically designed to overcome intrinsic limitations such as high curing temperatures and brittleness. Strategies reported in the literature include molecular design modifications (e.g., incorporation of flexible aliphatic chains or multifunctional benzoxazine structures), copolymerization with other thermosetting systems, nanocomposite-based approaches, and the use of catalysts or additives to precisely tailor curing behavior and optimize the thermomechanical and final mechanical performance of polybenzoxazine networks [8–10].

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The general synthesis of benzoxazine monomers typically proceeds via a condensation reaction involving a phenolic compound, a primary amine, and an aldehyde, a feature that affords remarkable flexibility in molecular design. The reaction progresses through the formation of intermediates that eventually lead to the cyclization and closure of the oxazine ring, resulting in the final benzoxazine structure [2, 3, 5, 7]. The different combinations of these reactants provide designers with the flexibility to tailor the monomer structure to the resulting polymer and, consequently, to the targeted final application.

In response to growing environmental and health concerns, as well as the demand for sustainable materials, significant efforts have been devoted to the development of bio-based benzoxazines derived from renewable resources. Natural phenolic compounds such as urushiol [11], guaiacol [12], cardanol [12, 13], and catechol [14], among others, have been successfully employed as alternatives to petroleum-based precursors, resulting in promising benzoxazine monomers. These studies highlight the versatility of such systems in advanced and sustainable polymeric materials. Nevertheless, challenges related to structural heterogeneity, limited reactivity, and processing difficulties remain.

Among renewable phenolic resources, cashew nutshell liquid (CNSL) and its main component cardanol have emerged as particularly attractive precursors for benzoxazine synthesis. The presence of a phenolic ring combined with a long aliphatic side chain offers unique opportunities to tailor polymer flexibility and processability [15]. This characteristic reduces the reliance on external flexibleness or complex chemical modifications often required for other bio-based phenolic precursors, making CNSL-derived benzoxazines particularly attractive for the development of sustainable, application-oriented materials. Previous studies, including the work of Stifani et al. [16], have already reported cardanol-based benzoxazine monomers, highlighting their structural feasibility and sustainable potential.

Nevertheless, despite these promising reports, the full potential of CNSL-derived benzoxazines in terms of structure and property relationships and application-driven performance has not yet been comprehensively explored, particularly for systems synthesized from cardanol and hexamethylenetetramine (HMTA). Herein, we report the use of cardanol and HMTA as starting materials for the synthesis of a benzoxazine monomer and present a comprehensive evaluation of its polymerization and thermal behavior.

Due to the known toxicity of formaldehyde, several alternative strategies have been explored to replace this reagent in the synthesis of benzoxazine monomers. One such alternative is the use of hexamethylenetetramine (HMTA), which effectively contributes to the formation of methylene bridges and introduces the nitrogen atom required for oxazine ring formation. This synthetic route represents a significant advantage by eliminating formaldehyde, a traditionally used but potentially hazardous compound. Building upon the methodology previously reported by Oliveira et al. [2], this study demonstrates the viability, reactivity, and efficiency of combining cardanol (Ca) and HMTA as a safer and more sustainable pathway for benzoxazine synthesis. However, the polymerization behavior of the obtained resin was not extensively investigated. In this work we report the curing behavior and polymerization characteristics of the synthesized cardanol-based benzoxazine resin.

One of the main challenges associated with benzoxazines is the high temperature required for their curing process (typically above 180 °C). This characteristic can limit the application of these resins in certain areas, especially where thermal control is crucial or where exposure to high temperatures can damage other sensitive components. Additionally, the high energy consumption and operational costs associated with prolonged heating are economically and environmentally disadvantageous.

To overcome the relatively high curing temperatures of benzoxazine resins, several modification strategies have been reported [17, 18], among which the use of Lewis acids has received considerable attention. Previous studies have demonstrated that Lewis acids based on metals such as aluminum, iron, zinc, and other inorganic systems can effectively catalyze the ring-opening polymerization of benzoxazines by activating the oxazine ring and facilitating phenolic reactions. In this context, Lochab et al. [19] reported the effect of catalysts on benzoxazine polymerization at low temperatures. Additionally, other studies have demonstrated significant reductions in curing temperature and associated changes in polymerization mechanisms [20–23].

Research is underway to develop more efficient curing methods at lower temperatures, which could significantly expand the use of benzoxazines in various industries and reduce their environmental impact. A promising example is the use of transition metal salts to reduce the curing temperature of benzoxazines, a strategy that has gained increasing attention in recent years. Although some studies have already explored the influence of metal salts on benzoxazine polymerization, the literature remains limited, especially regarding systems based on renewable monomers such as cardanol [24, 25].

Despite the extensive literature on cardanol-based polybenzoxazines and the wide range of reported modification strategies, limited attention has been paid to the polymerization behavior of benzoxazine resins synthesized from cardanol and HMTA. To the best of our knowledge, no previous studies have systematically explored the polymerization of HMTA-based benzoxazine resins.

Therefore, the present work aims to investigate the polymerization and curing behavior of a cardanol–HMTA benzoxazine resin, as well as to evaluate the thermal behavior and structural characteristics of the resulting polymers, thereby contributing to the development and understanding of sustainable high-performance polymeric materials.

Materials and methods

Materials

The reagents used in this work were purchased were used without prior purification. The solvents used were: hexane (C_6H_{14}, Synth 99%), ethyl acetate ($C_4H_8O_2$, Synth 99%), chloroform ($CHCl_3$, Synth 99%). The chemical reagents used in this work were: hexamethylenetetramine (HMTA) (Synth 99%), anhydrous sodium sulphate (Dinâmica 99%). Cardanol (90%), was provided by Amêndoas do Brasil LTDA (Brazil), magnesium chloride ($MgCl_2$, Sigma Aldrich 99%), aluminum chloride ($AlCl_3$, Sigma Aldrich 99%), zinc chloride ($ZnCl_2$, Sigma Aldrich 99%), iron chloride ($FeCl_3$, Vetec 99%).

Analytical methods

NMR spectra were obtained in a BRUKER advance DRX Nuclear Magnetic Resonance spectrometer (Billerica Massachustts, United States), operating at a frequency of 500 MHz for the 1H and 101 MHz for the 13C using deuterated chloroform (CDCl3). The Ca-c (30 mg) was dissolved in 450 µL of CDCl3 as a solvent in the dilution of the samples, with residual CHCl3 which was used as internal reference at 7.27 ppm and 77 ppm.

Fourier Transform Infrared Spectroscopy (FT-IR) was obtained in a PerkinElmer spectrometer model FTIR/NIR Frontier (Seer Green, England), using an ATR with ZnSe crystal surface in the range of wavenumber from 4000 to 550 cm−1 and the acquisition was performed with 32 scans.

Diffuse reflectance tests were performed using a Shimadzu UV-2600 UV-Vis spectrophotometer equipped with the ISR-2600Plus integrating sphere (Shimadzu Corporation, Kyoto, Japan).

The thermal behavior of the polymers was evaluated by Thermogravimetric Analysis (TGA) in a Mettler-Toledo analyzer TGA/SDTA851e (Schwerzenbach, Switzerland). For analysis, 5 mg of each sample were added to an alumina crucible. The samples were submitted to a heating program, in which the temperature ranged from 30 to 800 °C, at a heating rate of 10 °C min-1 under an atmosphere of N2 with a flow rate of 50 mL min−1.

Differential Scanning Calorimetry (DSC) analyses were performed in a Mettler Toledo DSC823e (Schwerzenbach, Switzerland). Samples (5 mg) were heated at a rate of 10 °C min−1 in a temperature range from 30 to 300 °C under N2 atmosphere and a flow rate of 50 mL min−1.

Synthesis of benzoxazine monomer

The synthesis of benzoxazine-HMTA (Ca-c) was carried out following the methodology described by Oliveira et al. with modifications [2]. In a beaker (250 mL), cardanol (50 g, 160 mmol) was added and heated to 80 °C, then HMTA (6.05 g, 43.2 mmol) was added, leaving the reaction under constant stirring at 100 °C for 4 h (Fig. 1). At the end of the reaction time, a viscous reddish-brown resin was obtained and used without further purification.

General procedure for ring-opening polymerization of Ca-c

Ca-c (3.0 g, 0.004 mol) was solubilized in 10 mL of ethyl acetate, then the salt ($MgCl_2$; $AlCl_3$; $FeCl_3$; $ZnCl_2$) previously dissolved in ethyl acetate was added in a proportion of 7.5% mol/mol.

The polymers of Ca-c/salts were obtained from the following protocol: approximately 2.0 g of Ca-c/salts were added to a silicone mold (40 × 20 × 2 mm) and polymerized at 70 °C 1 h, 100° C for 1 h, 120° C for 1 h, 150° C for 1 h and 180 °C for 1 h in a muffle furnace.

Gel content

The gel content (GC) of the polymers was calculated in accordance with ASTM D2765 [28], by immersing the polymers in chloroform for 24 h, and then drying in an oven, using Eq. 1 below:

$$Gel\ content\ (GC, \%) = \frac{W_t}{W_0} \times 100 \quad (1)$$

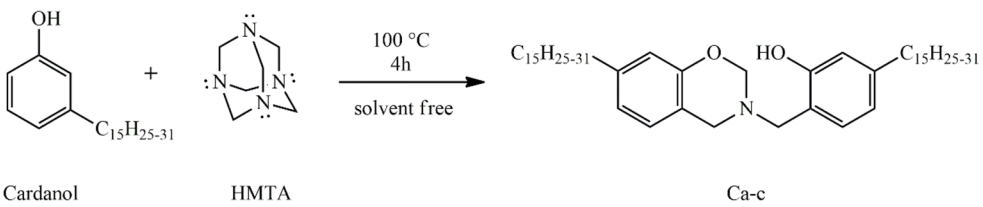

Fig. 1 Scheme of Ca-c synthesis

Where, W_0 is the initial weight of the specimen before the immersion in chloroform during 24 h and W_t is the weight of the specimen after immersion in the solvent.

Results and discussion

Structural characterization of cardanol-based benzoxazine

The chemical structure of the cardanol-based benzoxazine monomer (Ca-c) was confirmed by using FT-IR, ^{1}H and ^{13}C NMR analyses, as shown in Figs. 2, 3 and 4, respectively.

The main structural features of benzoxazine were initially assessed by FTIR analysis and the main structural aspects were compared to the starting material. Figure 2 shows their FTIR spectra, and the main assignments were carried out following the approach described by Oliveira et al. [2].

Figure 2 presents four highlighted absorption bands at 3350, 1500, 1240, and 968 cm^{-1}. The first one, at 3350 cm^{-1}, is related to the O–H stretching of the phenolic hydroxyl group present in the cardanol molecule. A significant reduction and broadening of this band can be observed in the spectrum of Ca-c. In the formed product, the presence of phenolic hydroxyl is evident, however, the corresponding band is barely visible due to the interaction between hydrogen and nitrogen in the oxazine ring, which promotes the formation of an intramolecular hydrogen bond [2].

The band in the 1500 cm^{-1} region is associated with the in-plane aromatic.

C–H skeletal mode characteristic of a trisubstituted benzene ring, indicating the occurrence of chemical modification in the aromatic ring [27].

The band at 1240 cm^{-1} corresponds to the asymmetric stretching mode of C–O–C due to the presence of the aromatic ether in the benzene ring [28]. Finally, the band at 970 cm^{-1} is associated with the presence of the N–CH_2–O group of benzoxazine, which can be attributed to the formation of the oxazine ring [29].

Figure 3 shows that there was a significant change in the structure of cardanol to benzoxazine that supported the success of the synthetic protocol. In the ^{1}H NMR region between 4 ppm and 6 ppm of Ca-c spectrum, it is possible to observe some signals (a, b and c) related to the new methylene groups originating from the oxazine ring (O-CH_2-N and the Ar-CH_2- N), and the Mannich bridge, respectively.

Both spectra display signals from 0.9 ppm to 3 ppm, attributed to the aliphatic hydrogens of the long alkyl chain in cardanol. Additionally, signals between 5 ppm and 6 ppm are associated with the olefinic hydrogens from the side chain.

In the ^{13}C NMR spectra of cardanol and Ca-c monomer, Fig. 4, it is possible to observe signals related to the oxazine ring with the chemical shift values at 80.72 ppm and 54.90 ppm. The signal corresponding to the methylene bridge is observed at 48.98 ppm.

The FTIR, ^{1}H NMR, and ^{13}C NMR analyses consistently confirmed the successful synthesis of the cardanol-based benzoxazine monomer (Ca-c). The observed bands and signals clearly indicate the formation of the oxazine ring and the

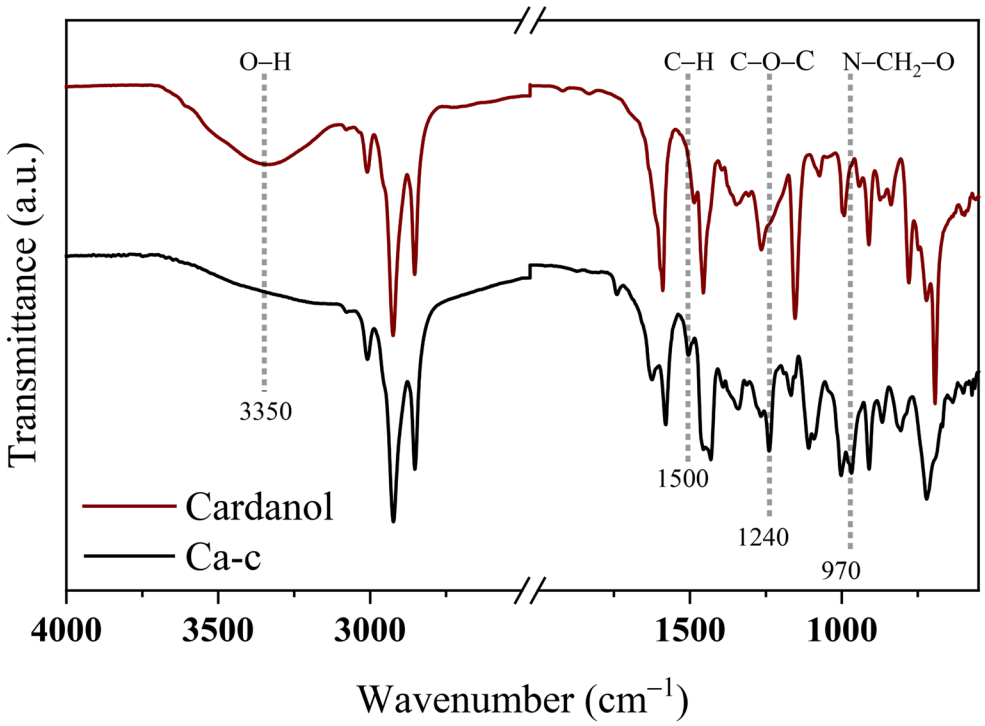

Fig. 2 FT-IR spectra of cardanol and Ca-c monomer

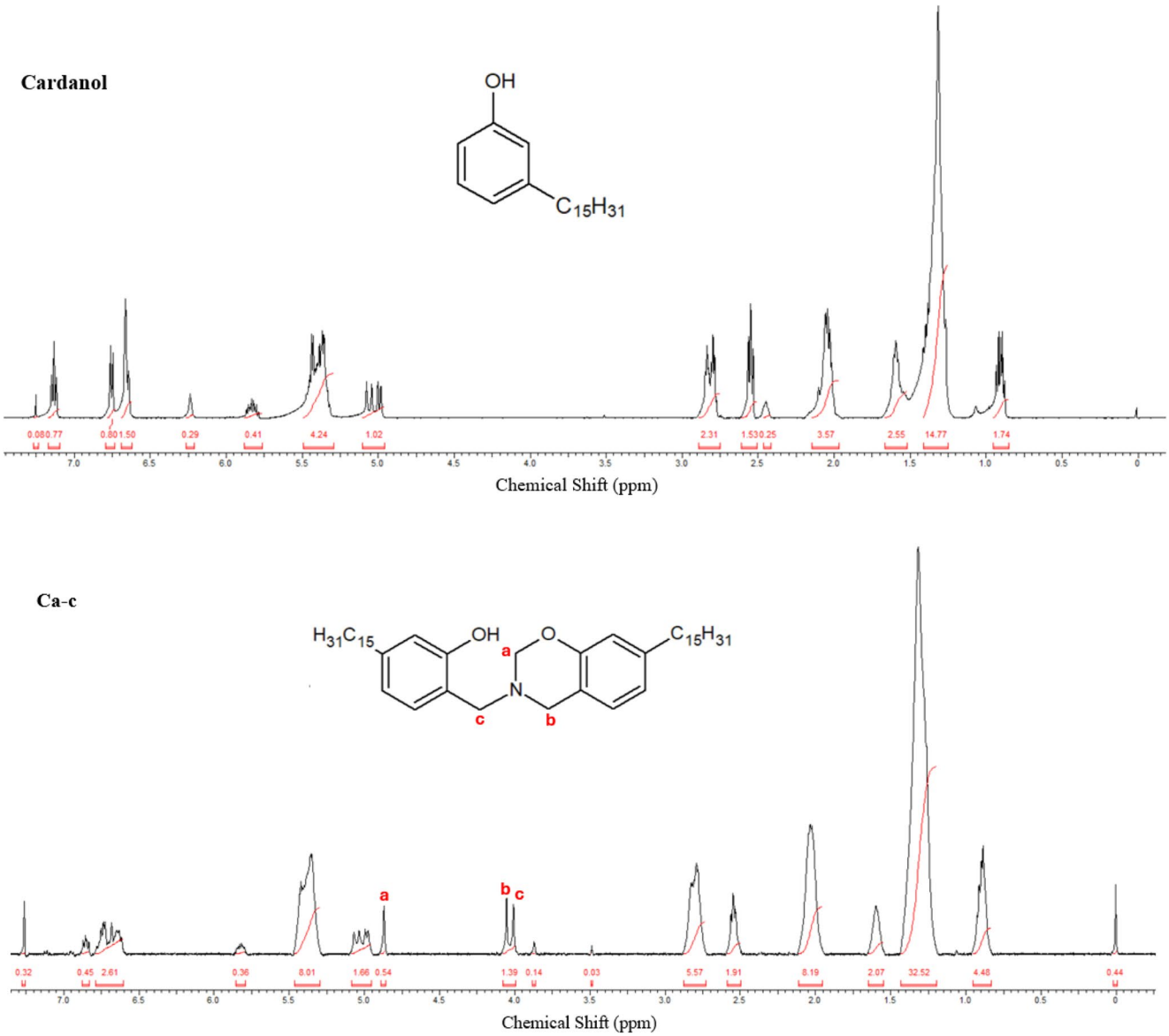

Fig. 3 ^{1}H NMR spectra of cardanol and Ca-c monomer

Mannich bridge, validating the structural modification of cardanol and the efficiency of the HMTA-based synthetic route.

Effects of lewis acids on the polymerization behavior of Ca-c

In order to assess the thermal behavior and polymerization properties of benzoxazine monomer, DSC was performed, as shown in Fig. 5, with the thermal parameters summarized in Table 1. The DSC of the neat monomer is also included for comparison.

The monomer Ca-c exhibited a single exothermic event associated with the ring-opening polymerization (ROP), with an onset polymerization temperature (T_{onset}) of 180 °C and a maximum polymerization peak (T_{max}) at 223 °C. Upon addition of various Lewis acids, significant alterations in the polymerization profile were observed, including shifts in both onset and peak temperatures.

The addition of Lewis acids promoted a shift of the exothermic peak towards lower temperatures, indicating a catalytic effect that facilitates the ROP reaction. For instance, the system containing $MgCl_2$ exhibited a T_{onset} reduced by 29 °C, while $AlCl_3$, $FeCl_3$ and $ZnCl_2$ 24 °C, 15 °C and 11 °C, respectively, compared to the neat monomer.

In general, Table 1 shows that increasing the cation hardness of Lewis acids enhances their ability to promote polymerization. In this study the hardness of each cation was estimated by Pearson model [30].

This effect occurs due to the stronger coordination between harder cations and oxygen atoms in the monomers.

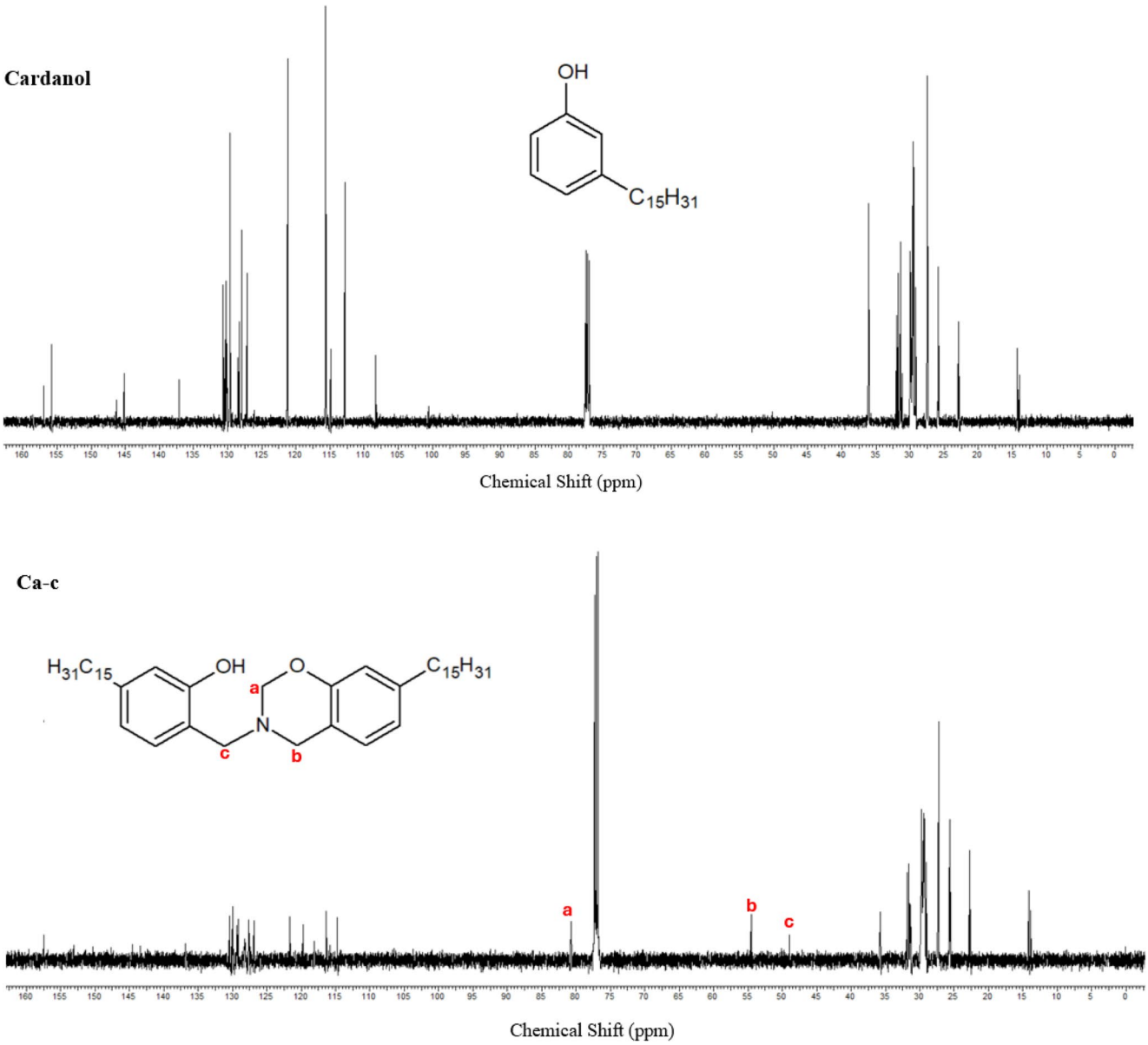

Fig. 4 ^{13}C NMR spectra of cardanol and Ca-c monomer

As the coordination strength increases, these oxygen-containing sites become more electrophilic, thus more reactive toward polymerization. When comparing the T_{onset} values of polymerization using Mg^{2+} and Al^{3+}, as well as for Fe^{3+} and Zn^{2+}, no significant differences are observed in the corresponding values.

When compared to other benzoxazine monomers and Lewis acids reported in the literature, metal chloride salts have been widely recognized as effective catalysts for the polymerization of benzoxazine [31]. Th

is catalytic activity is attributed to their Lewis acid character and ability to coordinate with heteroatoms in the monomer structure, such as nitrogen and oxygen. Although differences in the catalytic efficiency among these salts have been reported, even small molar proportions can significantly promote the ROP process.

Yang et al. [25, 14] observed a similar effect, reporting the appearance of an exothermic event when MClx salts were employed, consistent with the initiation of the polymerization reaction. These findings support the hypothesis that the interaction between Lewis acid centers and the oxazine ring facilitate the cleavage of the N-CH_2-O linkage, thus accelerating the process of polymer network formation.

Ran et al. [22] reported the polymerization of the benzoxazine monomer BA-a in the presence of $FeCl_3$, highlighting a mechanism based on coordination interactions. In this process, the Fe^{3+} ions, possessing vacant d-orbitals, can accept electron pairs from nitrogen and oxygen atoms within the

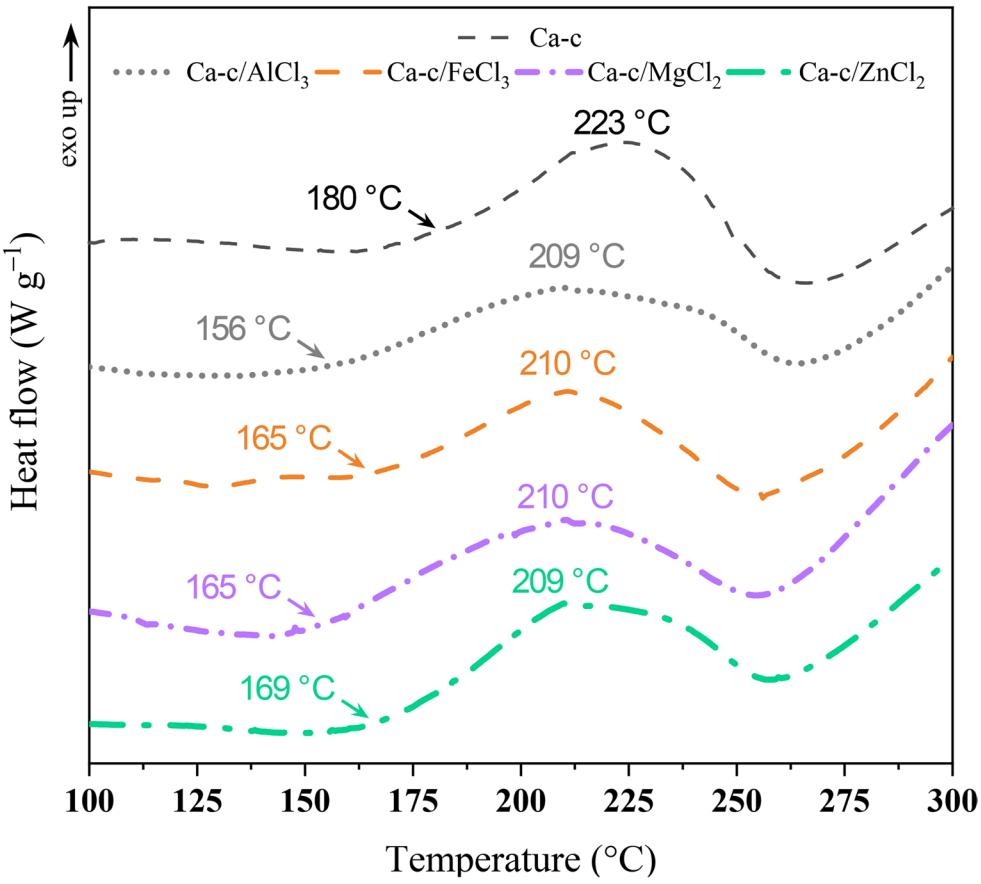

Fig. 5 Differential scanning calorimetry plots of pure benzoxazine and mixtures with 7.5% mol/mol various catalysts

Table 1 Thermal parameters of Ca-c and Ca-c/catalysts and cation hardness values for Lewis acids

Monomer	T_{onset} (°C)	T_{max} (°C)	ΔT_{onset} (°C)	Cation hardness (eV)
Ca-c	180	223	-	-
Ca-c/$AlCl_3$	156	209	24	45.8
Ca-c/$FeCl_3$	165	210	15	12.0
Ca-c/$MgCl_2$	151	210	29	32.5
Ca-c/$ZnCl_2$	169	209	11	10.8

oxazine ring. This interaction leads to the formation of coordinate bonds upon mixing $FeCl_3$ with BA-a, thereby facilitating the ring-opening polymerization.

A similar trend was observed in this study for benzoxazine Ca-c in the presence of $AlCl_3$, $FeCl_3$, $MgCl_2$, and $ZnCl_2$. Among these catalysts, $MgCl_2$ exhibited the most pronounced catalytic effect, leading to the greatest reduction in the onset polymerization temperature. Despite its relatively moderate Lewis acidity compared to $AlCl_3$ and $FeCl_3$, $MgCl_2$ likely forms favorable interactions with the benzoxazine structure, particularly through coordination with oxygen atoms, thereby efficiently activating the ROP process. This suggests that factors such as the ionic radius and coordination geometry of Mg^{2+} ions significantly contributed to its catalytic efficiency. As previously demonstrated by our group [32], the use of $MgCl_2$ significantly reduced the onset polymerization temperatures of various studied benzoxazines from cardanol.

In the case of the other catalysts used in this study, several factors may have contributed to their lower catalytic performance compared to $MgCl_2$. Possible competitive side interactions, aggregation phenomena, and the formation of less efficient coordination complexes may have occurred. Additionally, steric hindrance effects involving Al^{3+} and Fe^{3+} ions, as well as the lower Lewis acidity of $ZnCl_2$ and its less favorable interaction with the benzoxazine ring, could have limited the catalytic activity. As a result, the polymerization behavior in these systems was more like that of the neat monomer.

Overall, the results indicate that not only the Lewis acidity but also specific factors such as metal ion size, preferred coordination geometry, and interaction dynamics with the benzoxazine ring strongly influence the catalytic efficiency during the polymerization process. Moreover, the intrinsic chemical complexity and structural features of the benzoxazine monomer, such as the distribution and accessibility of coordination sites, also play a crucial role in modulating its interaction with Lewis acids and, consequently, the polymerization kinetics and the resulting network structure.

Summing up, Fig. 5 demonstrates that Lewis acids lower the T_{onset}, demonstrating their effectiveness as catalysts for renewable monomers such as cardanol, and enabling optimized curing and broader applications of these resins. These metal salts efficiently promote polymerization under milder conditions.

Based on the polymerization behavior observed in this study, the use of milder polymerization and curing temperatures is particularly advantageous, as it reduces energy consumption and enhances compatibility with temperature-sensitive substrates, thereby broadening the application window of CNSL-derived benzoxazine systems. These improvements directly influence potential applications by enabling the design of benzoxazine-based materials with tailored performance for coatings, adhesives, and composites while also offering benefits to end users in terms of reduced processing costs, improved sustainability, and enhanced material reliability.

Thermal properties of polybenzoxazines

The thermal stability of the polymers was evaluated using thermogravimetric analysis (TGA) and derivative thermogravimetry (DTG) under nitrogen atmosphere (N_2) (Fig. 6). The summarized results are presented in Table 2.

The TGA curves indicate that the thermal properties of the polymer without catalyst are comparable to those with Lewis acid catalysts. The pCa-c, pCa-c/$ZnCl_2$, pCa-c/$FeCl_3$ and pCa-c/$MgCl_2$ polymers presented high thermal stability with initial mass loss (T_{onset}) in the temperature range of 423 °C, 422 °C, 416 °C and 419 °C, respectively, while

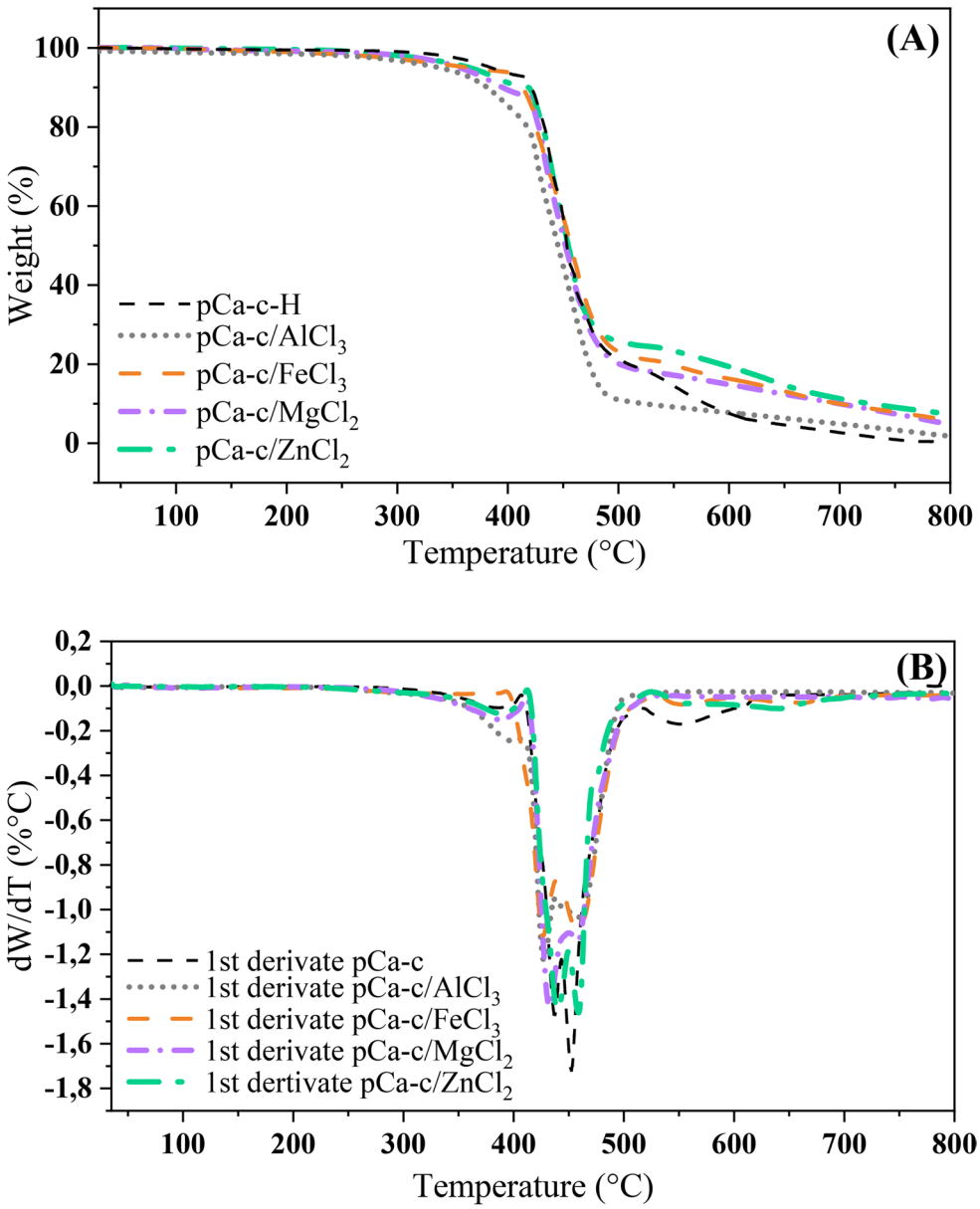

Fig. 6 (**A**) TGA and (**B**) DTG curves of cured benzoxazine resins with Lewis acid catalysts under N_2 atmosphere

Table 2 Thermal data of polybenzoxazines obtained by TGA and DTG analyses

Polybenzoxazines	T_{onset} (°C)	T_{max} 1st event (°C)	T_{max} 2nd event (°C)	dW/dT (%°C^{-1})	CY (%)
pCa-c	423	437	452	-0.0146	0.4
pCa-c/$AlCl_3$	411	427	458	-0.0109	10.7
pCa-c/$FeCl_3$	416	426	458	-0.0106	5.8
pCa-c/$MgCl_2$	419	432	459	-0.0129	4.7
pCa-c/$ZnCl_2$	422	439	459	-0.0135	7.4

pCa-c/$AlCl_3$ presented initial mass loss around 411 °C. Additionally, through the DTG curves, two events were observed for pCa-c and three events for pCa-c/catalysts. These events may be associated with the degradation of the polymeric structure influenced by the presence of the catalyst.

Polymers cured in the presence of Al^{3+} and Fe^{3+} showed lower T_{onset} and T_{max} values during the initial degradation stage, suggesting a milder thermal degradation behavior compared to the non-catalyzed polymer. Yang et al. [25, 14] reported a similar trend regarding T_{onset} values for metal ion-catalyzed curing of urushiol-based polybenzoxazine. On the other hand, Mg^{2+} and Zn^{2+} catalyzed polymers exhibited T_{onset} values of 419 °C and 422 °C, and T_{max} values of 432 °C and 439 °C, respectively. Among them, the Zn^{2+}-based polymer displayed the most significant mass loss during thermal decomposition.

Figure 6(B) and Table 2 also show that the intensity of the DTG curves (dw/dT) decreases for polymers cured in the presence of Al^{3+} and Fe^{3+}, suggesting that these ions reduce the degradation rate of the benzoxazine resins. This behavior can also be observed in the TGA curves (Fig. 6(A)), where the presence of these ions results in a smoother decay.

The greater mass loss observed in the Zn^{2+}-catalyzed polymer during thermal decomposition may be attributed to the formation of metal–ligand complexes that, while promoting polymerization, result in a polymer network that is less thermally stable [25]. The lower Lewis acidity of Zn^{2+}, compared to Al^{3+} and Fe^{3+}, may limit the degree of crosslinking and the thermal resistance of the resulting structure. As a result, during degradation, the polymer is more susceptible to bond cleavage, leading to a more significant mass loss.

The char yield of pCa-c at 800 °C was 0.39%. Upon incorporation of metal salts, a significant increase in char yield was observed for all catalyst-containing systems. Specifically, the char yields of pCa-c/$MgCl_2$, pCa-c/$FeCl_3$, pCa-c/$ZnCl_2$, and pCa-c/$AlCl_3$ increased to 4.74%, 5.79%, 7.35%, and 10.7%, respectively. This improvement suggests that the presence of Lewis acids contributes to the formation of thermally more stable structures, likely due to changes in the polymerization pathway or the formation of metal-associated degradation-resistant fragments.

These results reinforce the catalytic effect of the metal salts not only on curing efficiency but also on the thermal behavior of the resulting materials. From an end-user perspective, such advancements translate into materials that combine sustainability with improved durability, easier processing, and reduced reliance on petrochemical additives, thereby supporting the development of environmentally responsible and high-performance polymeric products.

In addition to the thermal and polymerization advantages discussed above, the environmental relevance of the proposed system can be considered from a qualitative perspective. Although quantitative metrics such as carbon footprint or biodegradability were not directly assessed in this study. Nevertheless, the use of cashew nut shell liquid, a renewable agro-industrial byproduct, combined with reduced reliance on petrochemical additives and the possibility of polymerization and curing at milder temperatures, suggests potential reductions in energy consumption and environmental impact during processing. These aspects reinforce the suitability of CNSL-derived benzoxazine systems for sustainable and application-oriented materials, while future studies will be directed toward quantitative environmental assessments to further substantiate these advantages.

Chemical structure analysis of polybenzoxazines

The FTIR analysis played a fundamental role in confirming the polymerization of the bio-based monomer. By identifying specific spectral changes —such as the disappearance of bands associated with the oxazine ring and ether groups, as well as the appearance of bands corresponding to phenolic and carbonyl groups — FTIR provided clear evidence of ring opening and the resulting chemical transformations. These findings highlight the effectiveness of FTIR as a powerful tool for monitoring structural changes during polymerization, as shown in Fig. 7.

From the spectra, the presence of phenolic groups resulting from the opening of the oxazine ring can initially be observed, evidenced by the broad band around 3360 cm^{-1} [29]. The disappearance of the band at 1500 cm^{-1}, attributed to the trisubstituted benzene ring [27] can also be noted.

The disappearance of the band at 1240 cm−1 is another indication of polymerization, as the C–O–C groups are converted into C–OH [28]. Additionally, the disappearance or reduction of the band at 970 cm−1, characteristic of the oxazine ring, is observed [29].

Specifically, in the pCa-c/FeCl3 and pCa-c/Zn2 spectra, the band at 1720 cm−1 related to C=O stretching can be observed, particularly in the former. The possible explanation for this difference lies in the oxidizing properties of Fe3+ and Zn2+, where some hydroxyl groups generated during polymerization may have been oxidized into carbonyl groups [25].

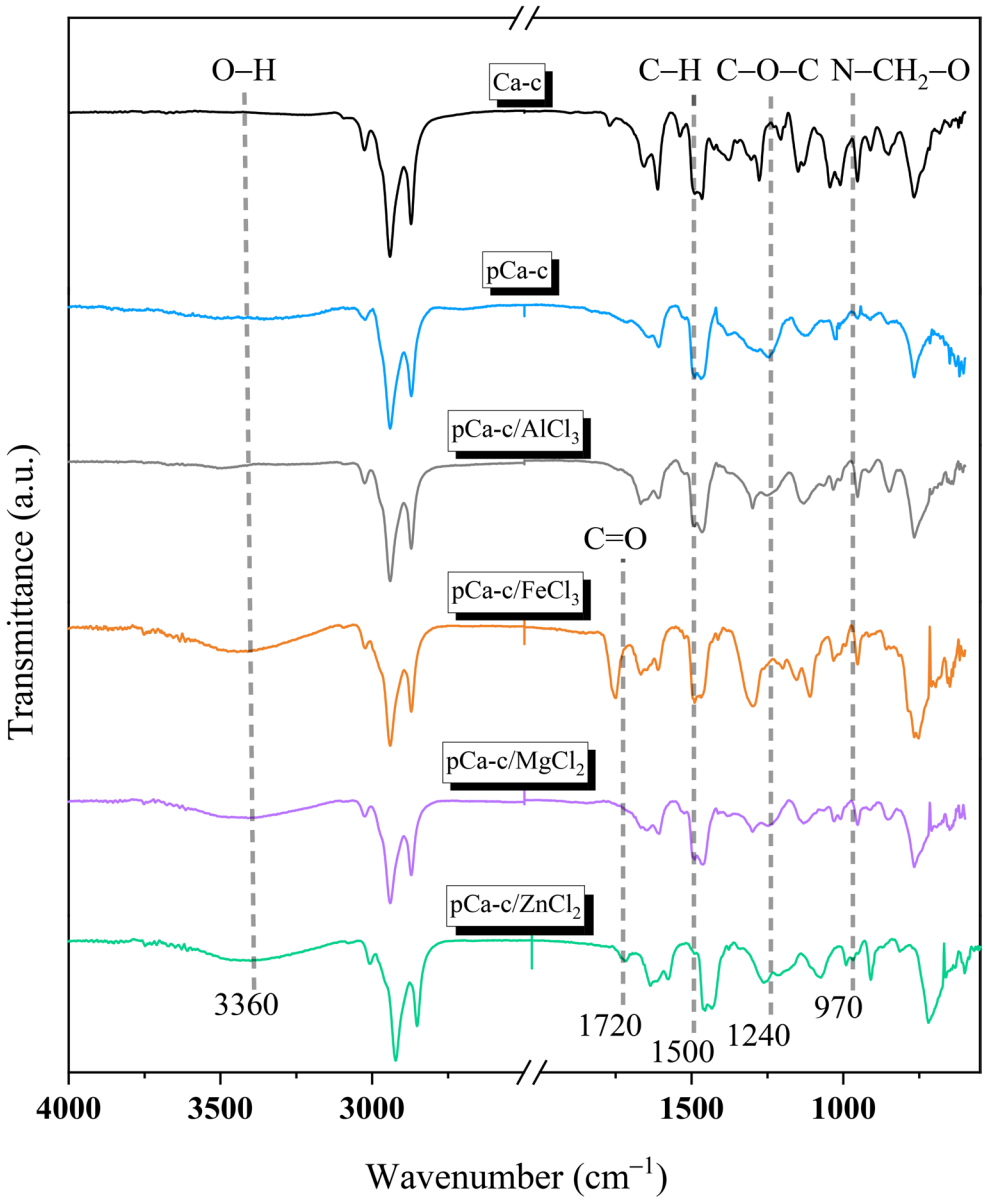

Fig. 7 FT-IR spectra of pCa-c and pCa-c/catalysts

The FTIR spectra indicates that polymerization occurred through the opening of the oxazine ring, with the formation of phenolic groups and the conversion of ether groups into hydroxyls. The disappearance of characteristic bands of the oxazine ring confirms its consumption. In the samples containing Fe^{3+} and Zn^{2+}, the presence of carbonyl groups suggests partial oxidation of hydroxyl groups, highlighting the influence of the metal on the final polymer structure.

Diffuse reflectance

The analysis of the diffuse reflectance of the polymers was conducted to investigate the influence of inorganic salts on the polymerization process of Ca-c, as shown by their spectra in Fig. 8.

It is observed that the polymers pCa-c, pCa-c/$AlCl_3$, and pCa-c/$MgCl_2$ exhibit only two bands in the N region, located at 283 nm and 338 nm. These bands are characteristic of n → π* electronic transitions, in which electrons from non-bonding orbitals (n) are promoted to antibonding orbitals (π*). This phenomenon is commonly observed in compounds containing heteroatoms such as nitrogen and oxygen, whose electronic configurations favor such spectroscopic transitions.

The pCa-c/$ZnCl_2$ polymer exhibits four well-defined bands in the diffuse reflectance spectrum, including the two previously mentioned N bands, as well as a B band at 428 nm, attributed to π → π* electronic transitions and a band in the Q region at 539 nm is observed, which is characteristic of excited states of lower energy.

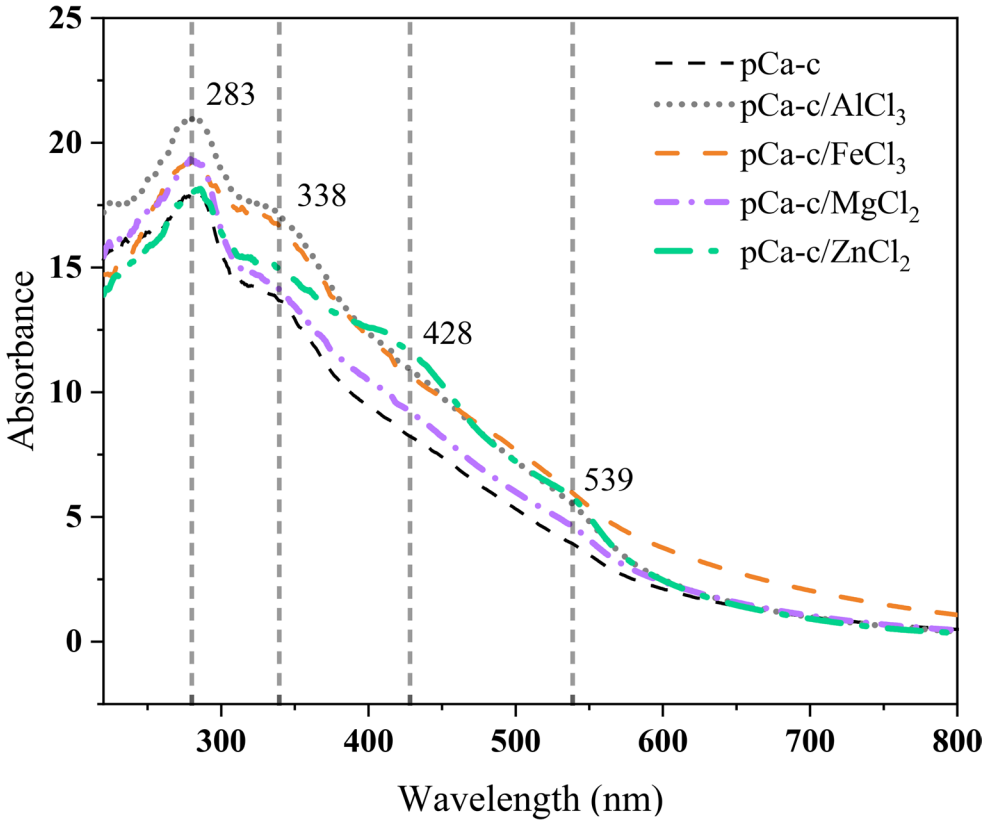

Fig. 8 Diffuse reflectance analysis of the polymeric samples

The absence of these additional bands in the $FeCl_3$ system indicates that, although coordinative interactions may occur, they are weaker or less stable, not forming a complexation like that observed with Zn^{2+}.

The difference in the behavior of the metals can be attributed to their electronic configurations and coordination capacities. Aluminum has an incomplete valence shell ([Ne] $3s^2$ $3p^1$), while magnesium ([Ne] $3s^2$) has its outermost shell filled. However, zinc ([Ar] $3d^{10}$), despite also having a filled valence shell, exhibits a larger atomic radius and consequently a higher electron density compared to magnesium due to the presence of a fully occupied d subshell. This characteristic gives Zn^{2+} a greater propensity for complex formation, as it belongs to the group of transition metals and can interact with ligand orbitals [33].

Therefore, the role of iron ([Ar] $3d^6$ $4s^2$) in the polymerization of Ca-c appears to be intermediate: Fe^{3+} acts as a Lewis acid, facilitating ring-opening and reducing the polymerization temperature compared to the neat monomer, but without establishing sufficiently strong or organized interactions to significantly alter the molecule' spectroscopic profile in the diffuse reflectance analysis. Its catalytic efficiency may be hindered by factors such as steric effects, aggregate formation, or low coordination selectivity with the active sites of Ca-c [34, 35].

While the presence of four bands in the diffuse reflectance spectrum suggests that zinc is effectively coordinated to the Ca-c molecule, forming a stable complex [25, 32]. The bands observed (Fig. 8) are characteristic of metal → ligand charge transfer, a phenomenon that requires higher energy to break these interactions. Consequently, the polymer containing zinc salt exhibited a higher polymerization temperature, as the dissociation of these bonds demands a greater energy input, Table 1.

On the other hand, magnesium and aluminum primarily act as catalysts, without establishing direct bonds with the Ca-c molecule [22]. This behavior reduces the activation energy of the polymerization process, allowing these polymers to be cured at significantly lower temperatures, as evidenced by previous results in this work, Table 1.

Conclusion

The cardanol-derived benzoxazine was synthesized using hexamethylenetetramine (HMTA) as a simultaneous source of methylene units and nitrogen atoms and subsequently cured in the presence of Lewis acids ($AlCl_3$, $FeCl_3$, $MgCl_2$, and $ZnCl_2$). The use of HMTA allowed the elimination of paraformaldehyde, thereby reducing the toxicity of the synthetic process.

Thermal analysis of the resulting polymer formulations demonstrated that the addition of metal salts significantly reduced the initial polymerization temperature (Tonset),

with the MgCl2-catalyzed system showing the highest catalytic efficiency, lowering the Tonset by up to 29 °C.

In addition to lowering the curing temperature, the catalysts directly influenced the crosslinking density and thermal properties of the resulting polymers. TGA analysis revealed that the salt-catalyzed polymers exhibited higher char yields, notably with $AlCl_3$ (10.7%), indicating the formation of denser and more thermally stable polymer networks. Diffuse reflectance spectroscopy further supported the presence of metal–ligand interactions, especially in the $ZnCl_2$ system, which showed additional bands associated with charge transfer, confirming the formation of coordination complexes. Therefore, the use of inorganic salts as catalysts proved to be an effective strategy for optimizing the curing process of benzoxazine resins, enhancing their thermal performance and expanding their potential applications in high-performance materials.

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Declarations

Ethics declarations and competing interests The author declares no competing interests.

References

1. Kotzebue LRV, De Oliveira JR, Da Silva JB, Mazzetto SE, Ishida H, Lomonaco D (2018) Development of fully biobased high-performance bis-benzoxazine under environmentally friendly conditions. ACS Sustain Chem Eng 6(4):5485–5494. https://doi.org/10.1021/acssuschemeng.8b00340
2. Oliveira JR, de Freitas DB, de Oliveira JFR, Mele G, Mazzetto SE, Lomonaco D (2021) New opportunity for sustainable benzoxazine synthesis: a straight and convenient one-pot protocol for formaldehyde-free bio-based polymers. Eur Polym J. https://doi.org/10.1016/j.eurpolymj.2021.110596
3. Microwave-assisted solvent-free synthesis of novel benzoxazines: a faster and environmentally friendly route to the development of bio-based thermosetting resins. J Polym Sci A Polym Chem 55(21):3534–3544. https://doi.org/10.1002/pola.28755
4. Oliveira JR et al (2020) Towards novel high-performance biocomposites: polybenzoxazine-based matrix reinforced with Manicaria saccifera fabrics. Compos Part B Eng.
5. Wang YX, Ishida EH (1999) Cationic ring-opening polymerization of benzoxazines, Polymer (Guildf) 40:4563–4570
6. Kotzebue LRV et al (2016) Spectral and thermal studies on the synthesis and catalyzed oligomerization of novel cardanol-based benzoxazines. Polymer 92:189–200. https://doi.org/10.1016/j.polymer.2016.04.005
7. Ribeiro FWM, Kotzebue LRV, Oliveira JR, Maia FJN, Mazzetto SE, Lomonaco D (2017) Thermal and mechanical analyses of biocomposites from cardanol-based polybenzoxazine and bamboo fibers. J Therm Anal Calorim 129(1):281–289. https://doi.org/10.1007/s10973-017-6191-x
8. Abdelkawy MA, Khedr AM (2026) Synthesis and characterization of polybenzoxazine–metal hybrids and evaluation of their thermal property. Polym Bull. https://doi.org/10.1007/s00289-025-06046-1
9. Lyu Y, Ishida H (2019) Natural-sourced benzoxazine resins, homopolymers, blends and composites: a review of their synthesis, manufacturing and applications. Prog Polym Sci 99:101168. https://doi.org/10.1016/J.PROGPOLYMSCI.2019.101168
10. Lochab B, Monisha M, Amarnath N, Sharma P, Mukherjee S, Ishida H (2021) Review on the accelerated and low-temperature polymerization of benzoxazine resins: addition polymerizable sustainable polymers. MDPI AG. https://doi.org/10.3390/polym13081260
11. Chen J et al (2021) Urushiol-based benzoxazine copper polymer with low surface energy, strong substrate adhesion and antibacterial for marine antifouling application." J Clean Prod. https://doi.org/10.1016/j.jclepro.2021.128527
12. Krishnan A et al (2025) , "Development of new bio-based shape memory hybrid polybenzoxazines through green strategy." Eur Polym J. https://doi.org/10.1016/j.eurpolymj.2025.113926
13. Ribeiro FWM, Kotzebue LRV, Oliveira JR, Maia FJN, Mazzetto SE, Lomonaco D (2017) Thermal and mechanical analyses of biocomposites from cardanol-based polybenzoxazine and bamboo fibers. J Therm Anal Calorim 129(1):281–289. https://doi.org/10.1007/s10973-017-6191-x
14. Kotzebue LRV, De Oliveira JR, Da Silva JB, Mazzetto SE, Ishida H, Lomonaco D (2018) Development of fully Biobased high-performance bis-benzoxazine under environmentally friendly

conditions. ACS Sustain Chem Eng 6(4):5485–5494. https://doi.org/10.1021/acssuschemeng.8b00340
15. Luo Y et al (2025) Research progress and application of solvent-free technology, green catalysis and biomass resource strategy for the synthesis of benzoxazine." React Funct Polym. https://doi.org/10.1016/j.reactfunctpolym.2025.106434
16. Calò E, et al (2007) Synthesis of a novel cardanol-based benzoxazine monomer and environmentally sustainable production of polymers and bio-composites. Green Chemistry 9(7):754–75. https://doi.org/10.1039/b617180j
17. Abdelkawy MA (2025) Eugenol-derived bio-based benzoxazine-co-urethane resins: synthesis, characterization and robust thermal stability. J Polym Res https://doi.org/10.1007/s10965-025-04457-2
18. Zhang S et al (2025) Catalytic polymerization of mono-benzoxazine functionalized phthalonitrile resin by lewis acids: mechanism and properties. J Appl Polym Sci https://doi.org/10.1002/app.57896
19. Lochab B, Monisha M, Amarnath N, Sharma P, Mukherjee S, Ishida H (2021) Review on the accelerated and low-temperature polymerization of benzoxazine resins: addition polymerizable sustainable polymers. Polymers. https://doi.org/10.3390/polym13081260
20. Zhang S, Ran Q, Fu Q, Gu Y (2019) Controlled polymerization of 3,4-dihydro-2H-1,3-benzoxazine and its properties tailored by Lewis acids. React Funct Polym 139:75–84. https://doi.org/10.1016/j.reactfunctpolym.2019.03.016
21. Liu C, Shen D, Sebastián RM, Marquet J, Schönfeld R (2013) Catalyst effects on the ring-opening polymerization of 1,3-benzoxazine and on the polymer structure. Polymer 54(12):2873–2878. https://doi.org/10.1016/j.polymer.2013.03.063
22. Ran QC, Zhang DX, Zhu RQ, Gu Y (2012) The structural transformation during polymerization of benzoxazine/ FeCl3 and the effect on the thermal stability. Polymer 53(19):4119–4127. https://doi.org/10.1016/j.polymer.2012.07.033
23. Liu C, Shen D, Sebastián RM, Marquet J, Schönfeld R (2011) Mechanistic studies on ring-opening polymerization of benzoxazines: a mechanistically based catalyst design. Macromolecules 44(12):4616–4622. https://doi.org/10.1021/ma2007893
24. Ishida H, Rodriguez EY, (1995) Catalyzing the curing reaction of a new benzoxazine-based phenolic resin, J Appl Polym Sci 58:1751–1760
25. Yang W, Xie Y, Chen J, Huang C, Xu Y, Lin Y (2022) Metal ion-catalyzed low-temperature curing of urushiol-based polybenzoxazine. Front Chem. https://doi.org/10.3389/fchem.2022.879605
26. (2016) Test methods for determination of gel content and swell ratio of crosslinked ethylene plastics, 1o de setembro de 2016, *ASTM International, West Conshohocken, PA*. https://doi.org/10.1520/D2765-16
27. Garigipati RKS, Malkapuram R (2020) Characterization of novel composites from polybenzoxazine and granite powder. SN Appl Sci. https://doi.org/10.1007/s42452-020-03333-6
28. Periyasamy T, Asrafali SP, Raorane CJ, Raj V, Shastri D, Kim SC (2023) Sustainable chitosan/polybenzoxazine films: synergistically improved thermal, mechanical, and antimicrobial properties. Polymers. https://doi.org/10.3390/polym15041021
29. Shutov VV, Bornosuz NV, Korotkov RF, Gorbunova IY, Sirotin IS (2022) Kinetics of benzoxazine and epoxy oligomer copolymerization. Thermochim Acta. https://doi.org/10.1016/j.tca.2022.179254
30. Pearson RG (1988) Absolute electronegativity and hardness: application to Inorganic Chemistry,
31. Kotzebue LRV et al (2016) Spectral and thermal studies on the synthesis and catalyzed oligomerization of novel cardanol-based benzoxazines. Polymer Guildf 92:189–200. https://doi.org/10.1016/j.polymer.2016.04.005
32. Mohamed MG et al (2014) Azopyridine-functionalized benzoxazine with Zn(ClO4)2 form high-performance polybenzoxazine stabilized through metal-ligand coordination. RSC Adv 4(92):50373–50385. https://doi.org/10.1039/c4ra08381d
33. Krężel A, Maret W (2016) The biological inorganic chemistry of zinc ions. Arch Biochem Biophys 611:3–19. https://doi.org/10.1016/j.abb.2016.04.010
34. Li A, Le Li J, Zhang JM, Ma JY, Wu eYX (2025) In situ synthesis of chemically stable hybrid co-networks of poly(thioctic Acid) with Fe3+via controlled/living cationic ring-opening polymerization. Macromol Rapid Commun 46(10). https://doi.org/10.1002/marc.202401115
35. Gopalaiah K (2013) Chiral iron catalysts for asymmetric synthesis. Chem Rev. https://doi.org/10.1021/cr300236r