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LLOYD RYAN VIANA KOTZEBUE

DEVELOPMENT OF BIO-BASED BENZOXAZINES DERIVED FROM AGROINDUSTRIAL RESIDUES FOR THE PRODUCTION OF HIGH-PERFORMANCE POLYMERS

FORTALEZA
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Tese de doutorado apresentada ao Programa de Pós-graduação em Química, do Centro de Ciências da Universidade Federal do Ceará, como requisito parcial para obtenção do Título de Doutor em Química. Área de Concentração: Química.

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This work is dedicated to my beloved sons, Christian and Adrian.

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“It doesn’t matter how many times you get knocked down. All that matters is you get up one more time than you were knocked down.” - Roy T. Bennett

RESUMO

As resinas termofixas são altamente desejadas em aplicações de compósitos poliméricos, especialmente para materiais poliméricos de alto desempenho que possuem propriedades mecânicas e térmicas elevadas. Entre as resinas que atendem a esses critérios, a resina de benzoxazina está conquistando seu espaço na arena de termofixos de alto desempenho devido às impressionantes propriedades térmicas e mecânicas de seu polímero, a polibenzoxazina. Como as resinas de benzoxazina de alto desempenho e comercialmente disponíveis são baseadas no tóxico bisfenol A (BPA), muitos tipos de pesquisas foram realizados para procurar materiais de partida alternativos para resinas de benzoxazina renováveis de alto desempenho. Buscando alinhar a química de benzoxazina com sustentabilidade, este trabalho se concentra no desenvolvimento de resinas de benzoxazina *bio-baseadas* de uma forma ambientalmente correta, seguindo, tanto quanto possível, os princípios da Química Verde. Após a produção dessas resinas, estas foram utilizadas para o desenvolvimento de polímeros renováveis de alto desempenho. Os capítulos 1 e 2 fornecem a introdução e a compreensão fundamental da química das benzoxazinas, das resinas termofixas e da necessidade de desenvolver estes dois tópicos de maneira sustentável. No Capítulo 3 é discutido o desenvolvimento de benzoxazina de bio-baseada utilizando derivados de lignocelulose (catecol e furfurilamina), como materiais de partida utilizando um método de síntese ambientalmente correto com o uso de irradiação de microondas como fonte de calor e poli(etilenoglicol) como solvente. Para validar este método de síntese para outros monômeros de benzoxazina, foi obtida também uma benzoxazina parcialmente *bio-baseada* utilizando BPA e furfurilamina. Estes monômeros foram copolimerizados em polibenzoxazinas, demonstrando elevadas propriedades térmicas e mecânicas, temperaturas de transição vítrea entre 290 e 350 ºC. No Capítulo 4 é discutida a utilização de recursos renováveis amplamente disponíveis para o desenvolvimento de resinas de benzoxazina *bio-baseadas* de alto desempenho e livres de BPA, utilizando o Líquido da Casca da Castanha de Caju (LCC) como materiais de partida. A resina obtida foi copolimerizada com a benzoxazina sintetizada anteriormente, a base de lignocelulose, em diferentes proporções e forneceram polibenzoxazinas com maiores temperaturas de transição vítrea e retardamentos de chama do que as resinas de benzoxazina à base de BPA.

Palavras-chave: catecol; LCC; polibenzoxazinas; poli(etilenoglicol); síntese assistida por micro-ondas; química verde.

ABSTRACT

Thermosetting resins are highly desired in polymeric composite applications, especially high-performance polymeric materials with high mechanical and thermal properties. Among the resins that fit these criteria, benzoxazine resin is conquering its space in the high-performance thermosetting resin arena due to the impressive thermal and mechanical properties of its polymer, polybenzoxazine, which can be higher than of the conventional thermosetting resins. As the high-performance and commercially available benzoxazine resins are based on the toxic bisphenol A (BPA), research has been performed on alternative starting materials for renewable high-performance benzoxazine resins. Looking forward to aligning benzoxazine chemistry with sustainability, this work focuses on developing bio-based benzoxazine resins in an eco-friendly manner, following as much as possible the principles of *Green Chemistry*. After the production of these resins, they were used to develop renewable high-performance thermosets. Chapter 1 and 2 provide the introduction and fundamental understanding of benzoxazine chemistry, thermosets, and the necessity to develop these two topics sustainably. Chapter 3 discusses the development of bio-based benzoxazine using lignocellulose derivates (catechol and furfurylamine) as starting materials by using an eco-friendly synthesis method, which compromises the use of microwave irradiation heating source and poly(ethylene glycol) as solvent. To validate this synthesis method for other benzoxazine monomers, a semi-bio-based benzoxazine was obtained using BPA and furfurylamine as starting materials. These two monomers were further copolymerized in different ratios into polybenzoxazines, demonstrating high thermal and mechanical properties, glass transition temperatures ranging from 290 to 350 °C, and good flame retardancies. Chapter 4 discusses the use of widely available renewable resources to develop high-performance and BPA-free bio-based benzoxazine resins by using Cashew Nut Shell Liquid (CNSL) as starting material. The obtained resin was copolymerized with the previously lignocellulose-based benzoxazine in different ratios, demonstrating polybenzoxazines with higher glass transition temperatures and flame retardancies than the BPA-based benzoxazine resins.

Keywords: catechol; CNSL; polybenzoxazines; poly(ethylene glycol); microwave-assisted synthesis; green chemistry.

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LIST OF ABBREVIATIONS AND ACRONYMS

^{13}C NMR	13C Nucleus Magnetic Resonance Spectroscopy
^{1}H NMR	1H Nucleus Magnetic Resonance Spectroscopy
CY	Char Yield at 800 oC
DMA	Dynamic Mechanical Analysis
DSC	Differential Scanning Calorimetry
DTG	Derivation of Thermogravimetric Analysis
FTIR	Fourier Transform Infrared Spectroscopy
LOI	Limiting Oxidation Index
PEG	Poly(ethylene glycol)
ROP	Ring Opening Polymerization
TGA	Thermogravimetric Analysis

LIST OF SYMBOLS

m.p.	melting point
T_o	Onset Polymerization Temperature
T_p	Peak Maximum Polymerization Temperature
T_D	Onset Degradation Temperature
T_5	Degradation Temperature at 5 % weight loss
T_{10}	Degradation Temperature at 10 % weight loss
T_{20}	Degradation Temperature at 20 % weight loss
T_{max}	Maximum Rate Degradation Temperature
ΔH_p	Enthalpy of Polymerization
E'	Storage Modulus
T_g	Glass Transition Temperature

SUMÁRIO

1 GENERAL INTRODUCTION

Polymeric materials are highly present around us, and their use has become essential for our daily lives due to their low-cost, easy processability, and a wide variety of applications. They can be found as textiles for our clothes, as plastic bags in the supermarket, or as lightweight materials for the frameworks of cars. Even though polymers are widely present in our environment, what are polymers exactly?

Polymers are macromolecules, molecules with relatively high molecular weights that can reach millions of Daltons. These are obtained by linking hundreds, thousands, or tens of thousands of basic units of usually low molecular weights (ODIAN, 2004). These basic units are generally called monomers, and the reaction process that transforms monomers into a polymer is called *polymerization*.

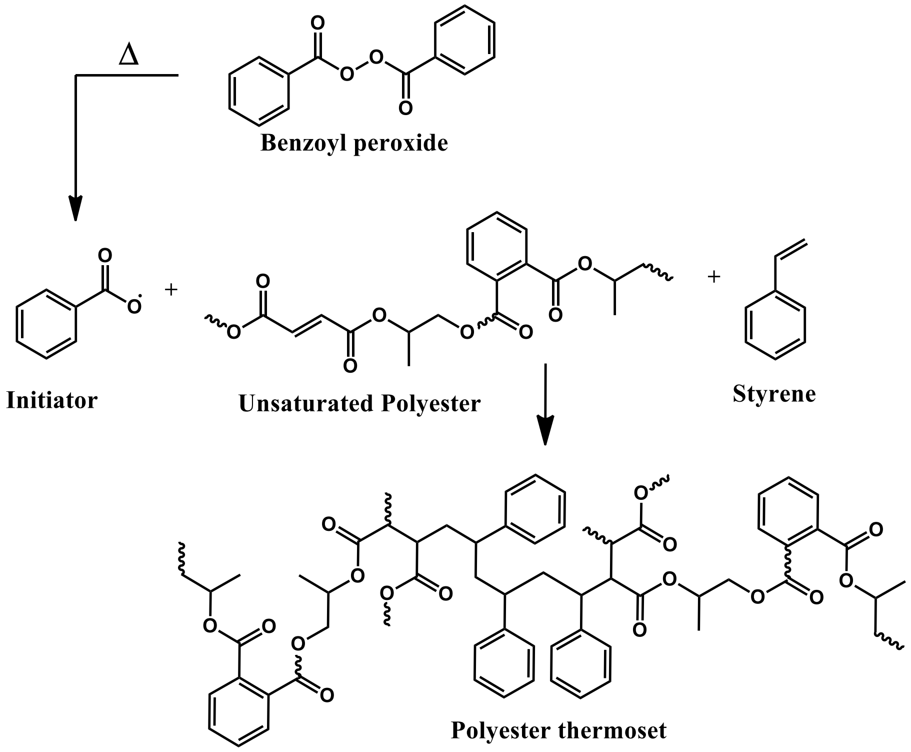
There are many ways to classify polymers, and one is regarded to their thermal behavior in thermoplastics and thermosets.

Thermoplastics are constituted of linear or branched-chain polymers, which give the ability to be soft or fusible when increasing heat, which turns them repeatedly remoldable. However, thermosets are constituted of highly cross-linked polymers making these infusible and insoluble.

Thermosets are frequently used for high-performance polymers that can maintain their thermal, mechanical, and chemical properties when exposed under extreme conditions such as high physical stress, high temperature, and corrosive materials (DE LEON et al., 2016). With such remarkable properties, these thermosets are widely used for adhesives, coatings, or matrices for polymer composites. Its precursors, thermosetting resins, are usually prepolymers that are mainly highly viscous or soft solid materials. The most known and commercially available thermosetting resins are unsaturated polyesters, phenolics, and epoxy.

Unsaturated polyester resins are polymers obtained after condensation of unsaturated acid or anhydrides and diols, where the unsaturations present along with the polymer chain act as cross-linking sites. The curing process of unsaturated polyesters, which is usually blended with styrene, can be performed through radical polymerization of the olefinic groups after catalytic decomposition of a peroxide, such as benzoyl peroxide (DHOLAKIYA, 2012; GAO et al., 2019)(Figure 1).

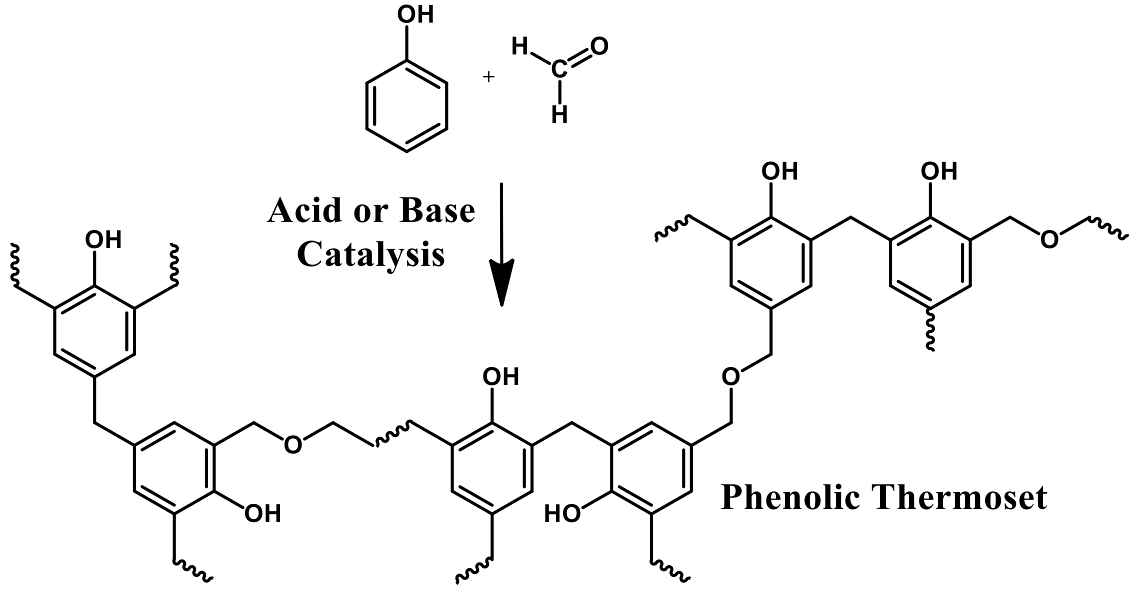
Figure 1 - Radical polymerization of unsaturated polyester resins



Source: The author

Phenolic resins gave birth to the first commercialized synthetic plastics under the name of bakelite. These resins are obtained by condensation polymerization of phenol and formaldehyde (Figure 2), where depending on the ratio used and the type of catalysis, two different kinds of phenolic resins can be achieved, which are resole (thermosetting resin) and novolac (thermoplastic resin) (XU et al., 2019). Resole resins are obtained using a formaldehyde/phenol ratio > 1 and after a base-catalyzed polymerization. The excess of formaldehyde favors cross-linking, and at high temperatures, this resin is cured into a very stable phenolic thermoset. However, novolac resins are obtained using a formaldehyde/phenol ratio < 1 and under acid-catalyzed polymerization. These novolac resins can be turned into a thermoset after reacting with a catalyst (SARIKA et al., 2020).

Figure 2 - General production of phenolic thermosets



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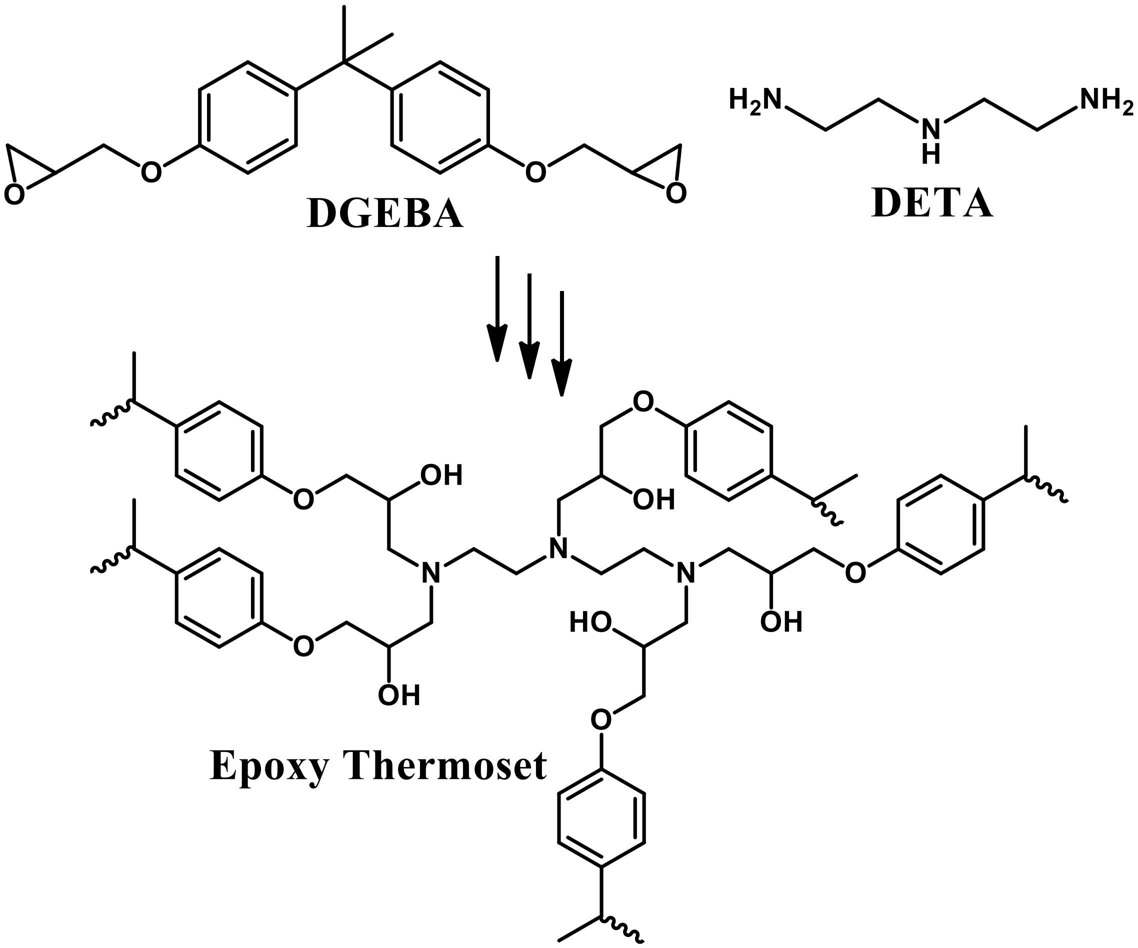
Epoxy resins are thermosetting materials that contain at least one epoxy function, which is reactive with other groups such as hydroxyls. The curing process of epoxy resins is through a ring-opening polymerization (ROP) which usually requires curing agents or hardeners, such as amines (RAQUEZ et al., 2010; VERMA et al., 2020). The most known and commercially available epoxy resin and hardener are diglycidyl ether of bisphenol A (DGEBA) and diethylenetriamine (DETA), respectively, and the combination of these two produce an epoxy thermoset possessing a highly crosslinked network (Figure 3)

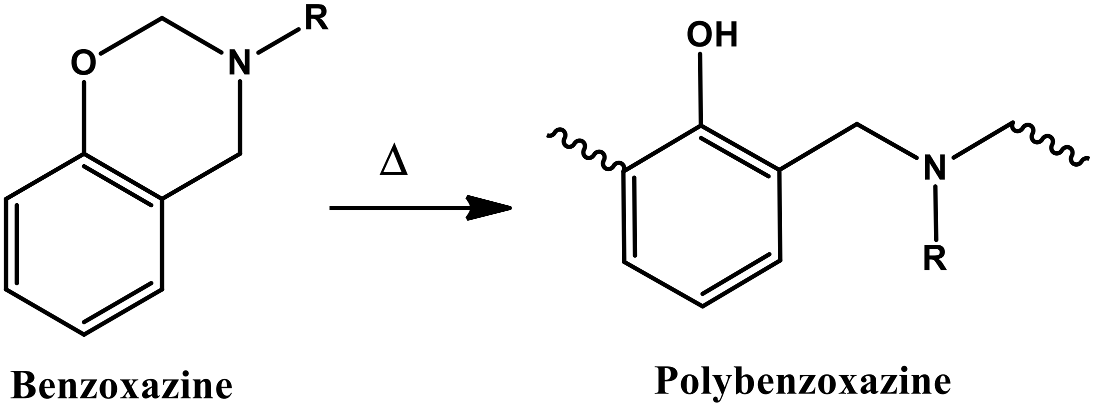
Figure 3 - Ring-opening polymerization of commercially available epoxy resin and hardener



Source: The author

These mentioned thermosetting resins are well studied and widely available. However, a new kind of thermosetting resin is gaining attention from academia and industry: benzoxazine (LYU; ISHIDA, 2019). After thermal ring-opening polymerization of this monomer into polybenzoxazine (Figure 4), the properties of the obtained polymer are a combination of the thermal properties and flame retardancy of phenolics with the mechanical properties of advanced epoxy systems (NAIR, 2004).

Figure 4 - Polymerization of benzoxazine



Source: The author

Another exciting aspect of benzoxazine resins is their great molecular design flexibility. Depending on the starting material used, mainly phenolics and primary amines, easy tailoring on the properties of the benzoxazine monomer and, consequently, the polymer can be made (KISKAN, 2018). Commercially available benzoxazines are classified as high-performance or fine chemicals and are usually derived from toxic bisphenol A (BPA). Since benzoxazine synthesis usually requires toxic solvents to avoid technical issues and uses long reaction times that can last hours or days under conventional heating, it is essential to develop eco-friendly synthetic methods and bio-based benzoxazine resins for renewable high-performance materials.

For the development of bio-based benzoxazines and polybenzoxazines, the use of biomass and biomass-derived starting materials for this purpose has been extensively reported (LYU; ISHIDA, 2019). Furfurylamine, a primary amine derived from platform chemicals of lignocellulose, has been used as starting material and demonstrated high thermal and mechanical stability of bio-based polybenzoxazines (LIU; CHOU, 2005). The use of catechol, a lignin-based phenolic, has not been reported to synthesize bio-based benzoxazines. However, according to the literature (DUMAS et al., 2016b), this phenolic compound demonstrates excellent potential for developing this kind of resin.

Another interesting renewable resource for phenolics for the development of bio-based benzoxazine is the widely available Cashew Nut Shell Liquid (CNSL), the main by-product of the cashew nut industries (LOMONACO; MELE; MAZZETTO, 2017). Cardanol, the main component of CNSL, has already been used to develop bio-based polybenzoxazines (MONISHA et al., 2019). However, their properties are not ideal for high-performance materials as they demonstrate low thermal and mechanical properties. Even though that raw CNSL has already been used for benzoxazine synthesis (A. ATTANASI et al., 2012), no study was performed on its respective polybenzoxazine.

Looking forward to developing an eco-friendly synthetic method for bis-benzoxazine synthesis, the use of neoteric solvents and alternative heating sources are viable options. As a neoteric solvent, poly(ethylene glycol), also known as PEG, can be used as a non-toxic and inert solvent. And owing to its capability to absorb microwave irradiation, this electromagnetic wave can also be used as an excellent heating source, providing high yields and short reaction time (KAPPE, 2004; OLIVEIRA et al., 2017).

Therefore, looking forward to substituting BPA-based benzoxazines, the purpose of this study is to develop novel high-performance bio-based benzoxazines by using lignocellulose-derived chemicals and CSNL as starting materials. To make the benzoxazine synthesis sustainable, these renewable resins were generated using PEG as a non-toxic neoteric solvent and microwave irradiation as a heating source.

2 LITERATURE REVIEW

Thermosetting polymers

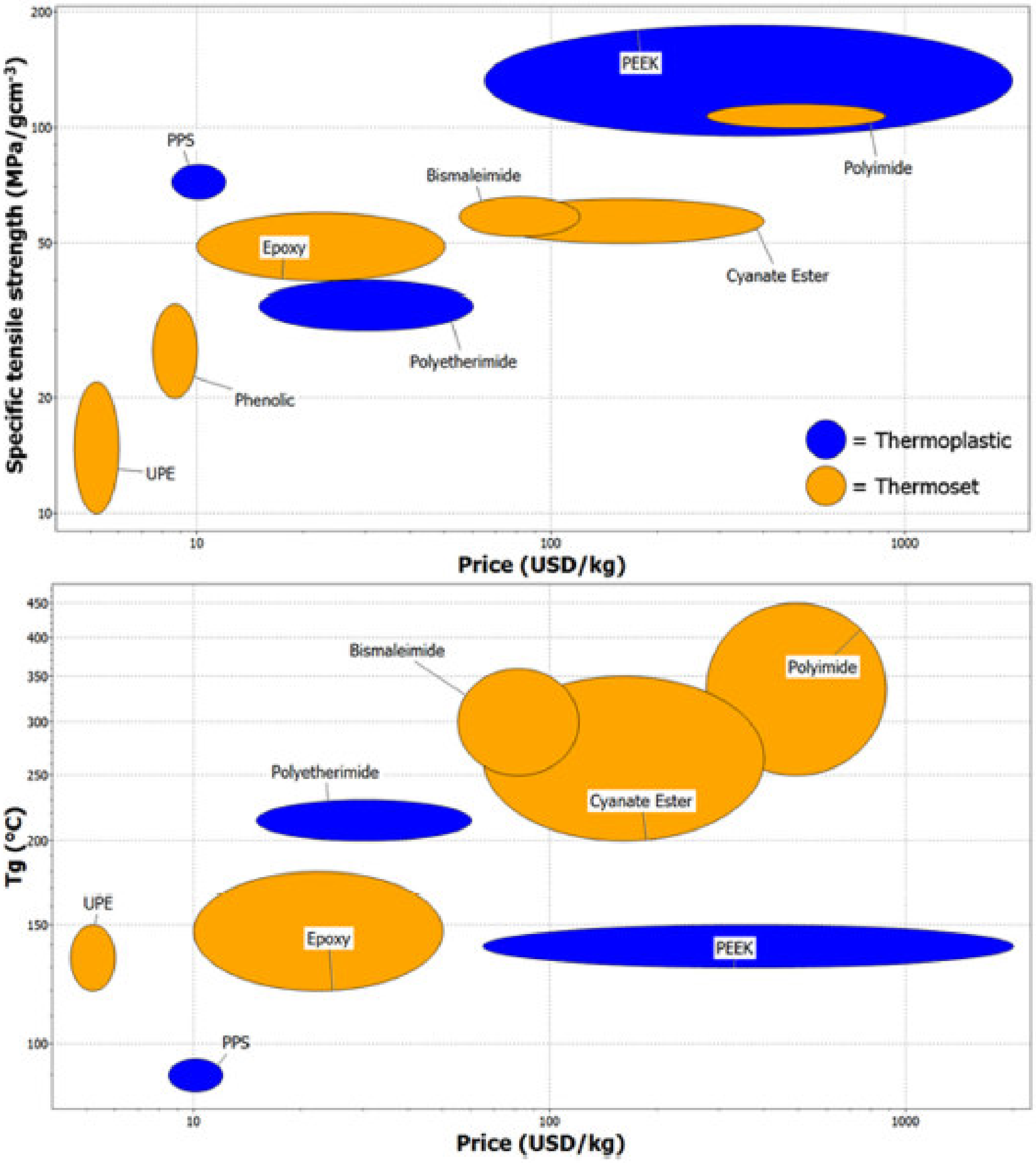
Thermosetting polymers, also known as thermosetting resins, are prepolymers in a solid or viscous state that turn into an infusible and insoluble polymer, also known as thermoset, after going through a curing process. After curing, which is cross-linking between one polymer chain with another into a polymer network, these resins turn into thermosets with high modulus, high thermal stability, high electrical and chemical resistance (RAQUEZ et al., 2010). It is not surprising that these thermosets are used as high-performance polymers with such extraordinary properties.

These properties make thermosetting resins desirable for polymer composite manufacturing companies with applications ranging from civil infrastructure and transport (RAQUEZ et al., 2010). For example, in civil infrastructure, there is a growing interest in concrete-polymer composites in constructions (VAN GEMERT et al., 2005) and for the production of wind turbine blades (MAMANPUSH et al., 2018). In transportation, the growing demand for polymer composites focuses on primary or secondary structures for automotive (KHAN et al., 2018), maritime (TRAN; NGUYEN; LAU, 2018), and aerospace (ALTIN KARATAŞ; GÖKKAYA, 2018; ZHU; LI; CHILDS, 2018) engineering.

Nowadays, polymer composites can be composed of a variety of thermosetting polymers with different mechanical and thermal properties, and their costs can be quite low till reaching thousands of dollars per kg (IREDALE; WARD; HAMERTON, 2017) (Figure 5). The most known and commercialized thermosetting polymers are unsaturated polyesters, phenolics (novolac and resole), and epoxies due to their low cost and the wide demand where elevated temperatures are not required. For example, epoxy resins can possess similar specific tensile strength compared with bismaleimide and cyanate esters, showing that the former is a better option than the latter resins for coating application (for example, seamless flooring) or composite fabrication of wind turbine blades. In other words, for applications that do not require high thermal properties, epoxy resin is a suitable choice.

However, for applications where high thermal *and* mechanical properties are necessary, the use of high-performance thermosetting resins such as epoxies, bismaleimides, cyanate esters, and polyimides (IREDALE; WARD; HAMERTON, 2017) are highly desired.

Figure 5 – Comparison of the glass transition temperature and price of advanced resins



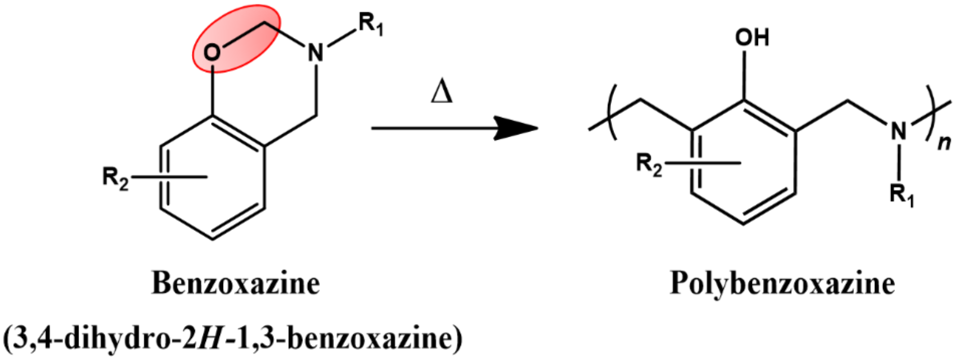
Source: IREDALE; WARD; HAMERTON, 2017

Now there is a new class of thermosetting resins conquering his space in the market of high-performance materials, which is benzoxazine.

Benzoxazines and Polybenzoxazines – New thermosetting resins for high-performance polymers

Benzoxazines contain a benzene ring fused with an oxazine ring, a heterocyclic six-membered ring containing one nitrogen and one oxygen atom. At high temperatures, the 3,4-dihydro-2*H*-1,3-benzoxazine, called benzoxazine hereafter, polymerizes into polybenzoxazines through a ring-opening polymerization process (ROP) after the cleavage of the C-O bond (Figure 6). In 1994, Ning and Ishida reported for the first time studies on the polybenzoxazine properties (NING; ISHIDA, 1994a, 1994b), where these polymers exhibit impressive high strength and glass transition temperatures, making them suitable for high-performance thermosets.

Figure 6 - Polymerization scheme of benzoxazine



Source: The author

Besides their excellent thermomechanical stability and typical properties of conventional thermosets, polybenzoxazines also possess good flame retardancy, including halogen-free (AMARNATH; APPAVOO; LOCHAB, 2018; PERIYASAMY; ASRAFALI; KIM, 2017), and low surface energy, even lower than TEFLON (WANG et al., 2006a, 2006b; ZHANG et al., 2018). And compared with conventional thermosetting resins, the polymerization of benzoxazine resins also has advantages: (a) no requirement of an initiator or catalyst; and (b) low volume shrinkage after polymerization.

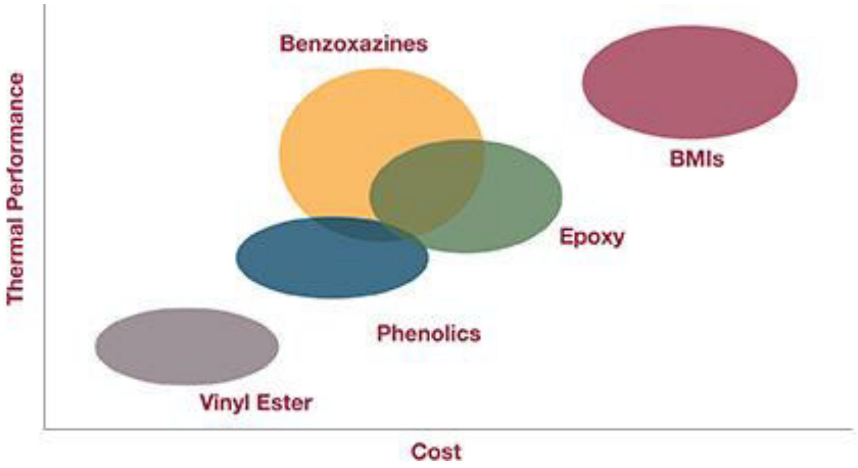
Another attractive property of benzoxazine is its high flame retardancy, which is the ability of a material to avoid or slow the growth of a fire. One of the techniques to study this property is by determining the *Limiting Oxidation Index (LOI),* the minimum oxygen-nitrogen mixture necessary to maintain the combustion of a material after ignition. Flammable materials possess *LOI* values ≤ 26, and an impressive way to estimate the LOI values is by using the van Krevelen equation (VAN KREVELEN, 1975):

$$LOI = 17.5 + 0.4\,(CY) \qquad \text{(Equation 1)}$$

This equation is validated for halogen-free polymeric materials, and it correlates the obtained char yield values of TGA analysis with the LOI values.

All these interesting properties described of polybenzoxazines have drawn much attention from academia and industry and made it a strong competitor for high-performance materials. Compared with traditional thermosetting resins (Figure 7), benzoxazine resins have a better thermal-performance/cost-benefit than phenolics and epoxies. Bismaleimides (BMIs) can possess superior thermal performance than benzoxazines, however, benzoxazines have an advantage to its lower cost and the possibility to produce polybenzoxazine in an out-of-clave method.

Figure 7 - Comparison of benzoxazine resins with conventional thermosetting resins

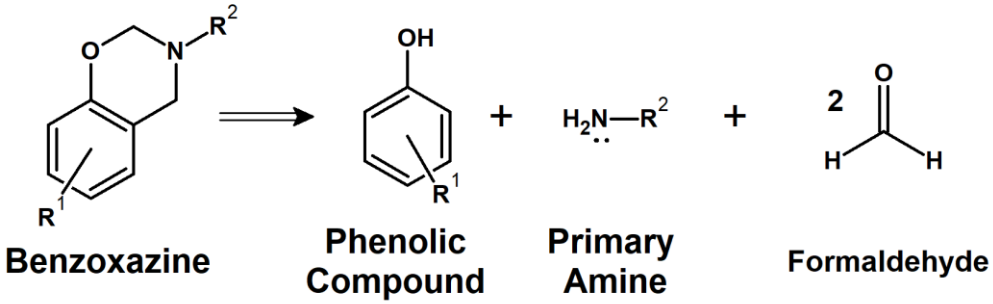


Source: (HUNTSMAN, 2018)

Molecular Design Flexibility of Benzoxazine

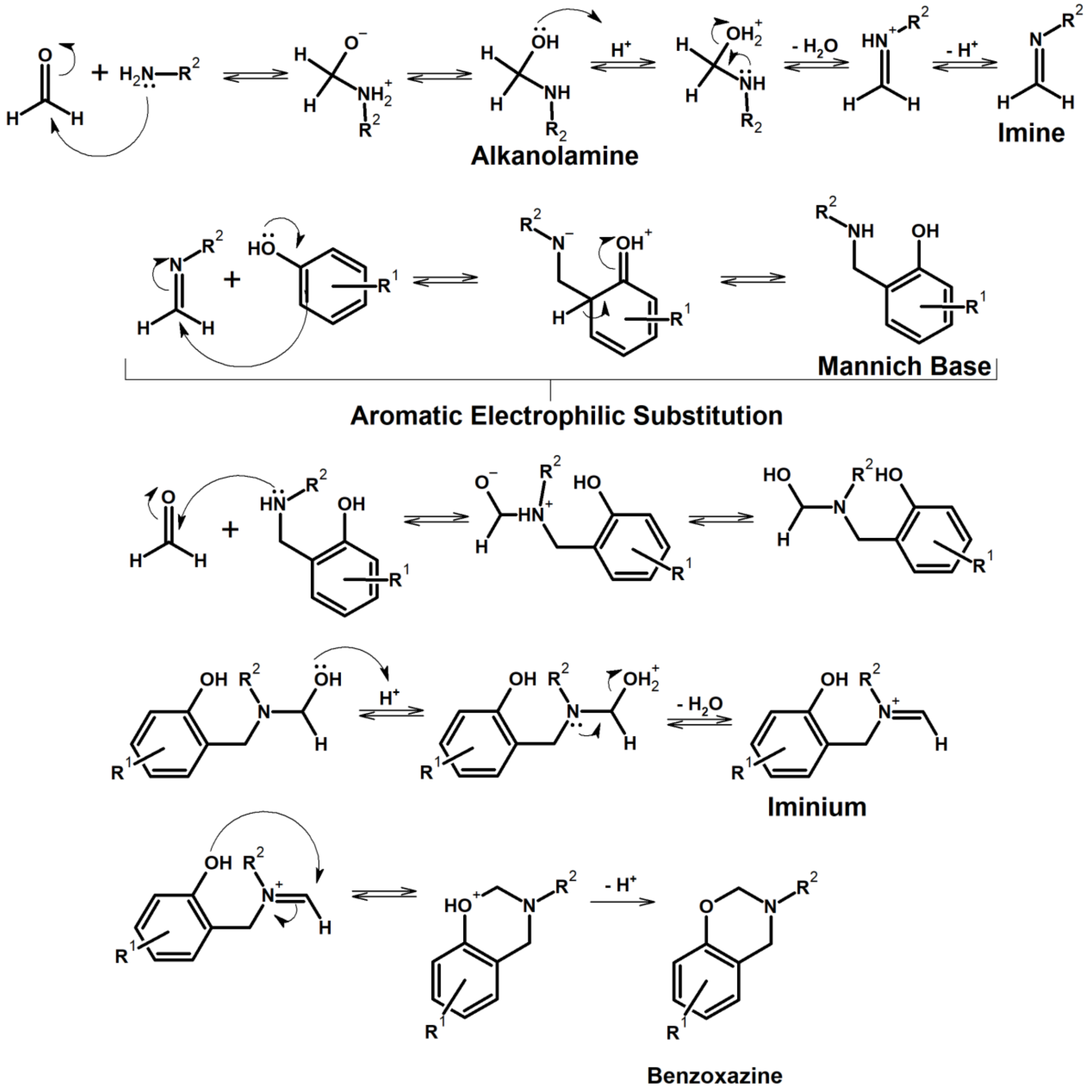
The synthesis of benzoxazine was first reported in 1944 by Holly and Cope (HOLLY; COPE, 1944). But from the late 1940s till the mid-1960s, Burke and coworkers (BURKE, 1949; BURKE et al., 1965; BURKE; GLENNIE; WEATHERBEE, 1964; BURKE; MURDOCK; EC, 1954; BURKE; SMITH; WEATHERBEE, 1952; BURKE; STEPHENS, 1952; BURKE; WEATHERBEE, 1950) made a significant contribution in understanding the benzoxazine chemistry. The benzoxazine monomer can be obtained from a phenolic compound, a primary amine, and formaldehyde (Scheme 1), and the proposed mechanism of benzoxazine synthesis is shown in Scheme 2.

Scheme 1. Benzoxazine and its starting materials



Source: The author

Scheme 2 - Proposed mechanism of benzoxazine synthesis

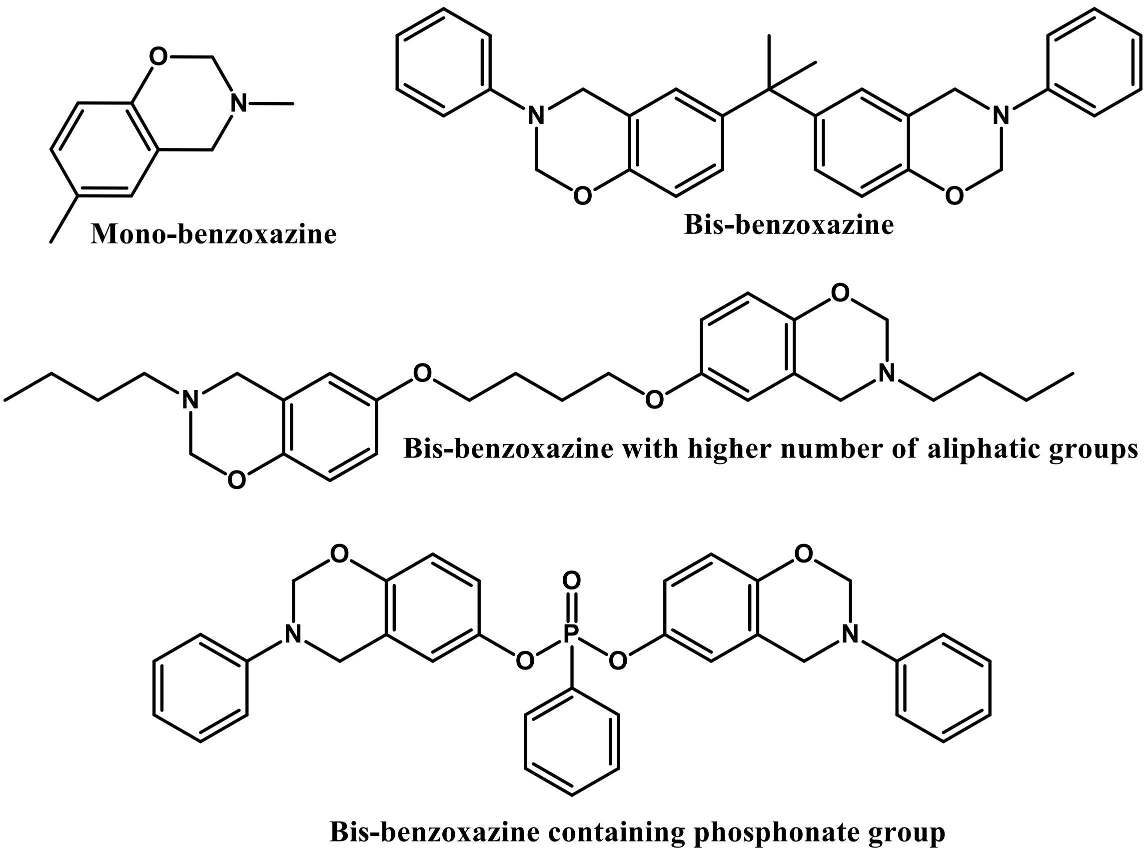


Source: The author

The primary amine performs an addition reaction with formaldehyde to form an alkanolamine, which transforms later into an imine after condensation. The phenolic compound with a free ortho-position suffers an electrophilic aromatic substitution with this imine, forming a Mannich base. The secondary amine of the Mannich base reacts with another formaldehyde molecule, following the same mechanism as described before, till transforming into an iminium ion. This electrophilic ion is reactive enough to be attacked by the hydroxyl group of the phenolic compound, closing the oxazine ring, obtaining the benzoxazine.

Benzoxazine synthesis has great molecular design flexibility, which means a wide variety of benzoxazine monomers can be synthesized depending on the use of their starting materials (BARANEK et al., 2012; CHOI et al., 2006; NING; ISHIDA, 1994a; REISS et al., 1985) (Figure 8). In the point of view of material science, the molecular design flexibility of benzoxazine synthesis provides easy tailoring on the properties of the monomers and, consequently, the properties of its respective polymer. This molecular design flexibility is undoubtedly an advantage when it is necessary to synthesize specific monomers and/or polymers containing particular properties for the desired application.

Figure 8 - Different benzoxazine monomers



Mono-benzoxazine

Bis-benzoxazine

Bis-benzoxazine with higher number of aliphatic groups

Bis-benzoxazine containing phosphonate group

Source: BARANEK et al., 2012; CHOI et al., 2006; NING; ISHIDA, 1994a; REISS et al., 1985

For example, mono-benzoxazines, also known as monofunctional benzoxazines, contain only one oxazine ring in a monomer. These monomers are usually not suitable for high-performance material applications as they provide generally oligomerized benzoxazine (REISS et al., 1985), barely forming crosslinks from one polymer backbone with another. If an initiator is used for the thermal polymerization of mono-benzoxazine, thermoplastic polybenzoxazine can be produced (WANG; ISHIDA, 2000). Therefore, a strategy to use benzoxazine for high-performance materials is by increasing the number of oxazine rings in one monomer, such as bis-benzoxazines.

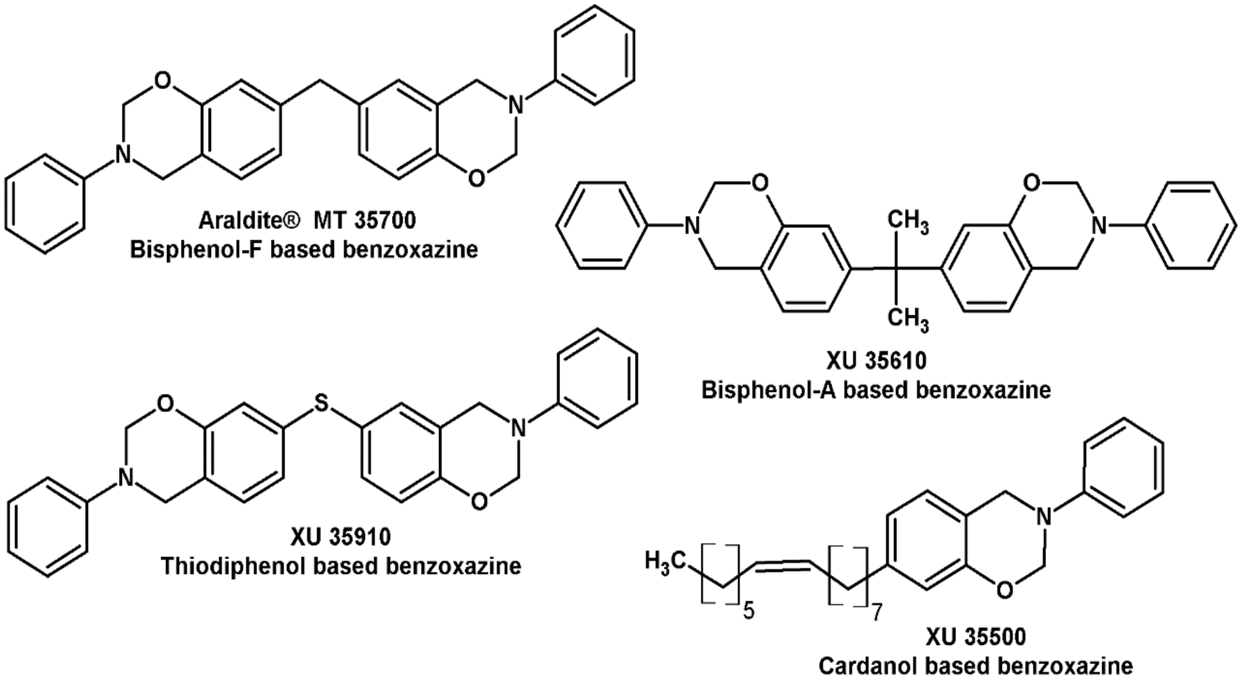
Bis-benzoxazines (Figure 8), also known as bifunctional benzoxazines, are benzoxazine monomers containing two oxazine rings. They can be obtained by using a bisphenol with two equivalents of primary amine and four equivalents of formaldehyde. The increase of oxazine rings in one monomer favor cross-linking, forming high molecular weight polymers, making them suitable as high-performance thermosetting resins (NING; ISHIDA, 1994a, 1994b).

The presence of certain groups in the chemical structure of the benzoxazine also alters the properties of the monomers and the polymers. The more aliphatic groups are available in the monomer, the better the processability of the monomer, the higher the plasticity, and the lower the thermal and mechanical resistance of the polymer (BARANEK et al., 2012). If an increase of thermal stabilities of polybenzoxazine is desired, this can be achieved by incorporating a phosphonate group in the benzoxazine monomer (CHOI et al., 2006).

Commercially Available Benzoxazine Resin

Even though more than two decades of studies have been conducted on benzoxazines and polybenzoxazines, since the first publication of the superb properties of polybenzoxazines (NING; ISHIDA, 1994a), benzoxazine resins still have a reduced market. Most of the commercially available benzoxazine resins are bis-benzoxazines. Companies like Huntsman and Shikoku have a vast collection of benzoxazine resins, being classified as high-performance components (Figure 9) (HUNTSMAN, 2018) or fine chemicals (SHIKOKU, 2018). Polybenzoxazines can reach flexural moduli ranging from 4.5 to 5.3 GPa (HUNTSMAN, 2018; SHIKOKU, 2018), 76 to 104 % higher than the epoxy thermosets (SHIKOKU, 2018). And the flame retardancy of benzoxazine resins is also a desired property for high-performance materials. Shikoku provides a benzoxazine resin named **P-d,** the only resin with the same flame resistance as an epoxy resin containing 40% (w/w) of a phosphorous flame retardant additive (SHIKOKU, 2018).

Figure 9 - Molecular structures of benzoxazine products of Huntsman

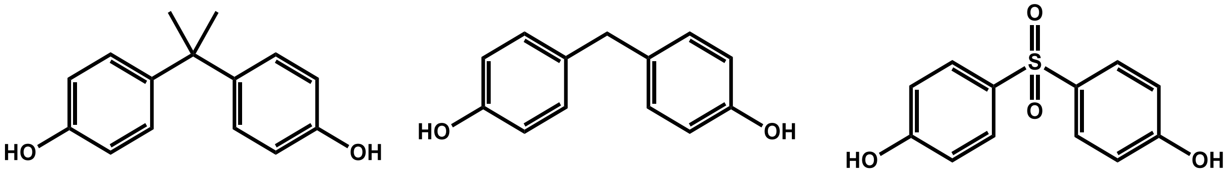


Source: HUNTSMAN (2018)

Environmental Concerns of Benzoxazine Synthesis

Bis-benzoxazine synthesis has some environmental issues that need to be dealt with. As it can be seen in Figure 9, most of the commercial benzoxazine resins are based on bisphenol A (BPA) or its analogs, bisphenol F (BPF) and bisphenol S (BPS) (Figure 10). Even though XU 35500 is presented as a “green” benzoxazine from the company, this product possesses 20 % of the cardanol-based benzoxazine and 80 % of XU 35610, which shows the production of these commercially available high-performance resins requires a high demand of BPA.

Figure 10 - Chemical structure of BPA and its analogs



Bisphenol A
(BPA)

Bisphenol F
(BPF)

Bisphenol S
(BPS)

Source: The author

BPA is considered one of the essential chemicals in the world due to its low-cost, high purity, and high availability and its annual production of 4.5 million tons (TRITA et al., 2017). This bisphenol has gained serious restrictions due to its toxicity since it acts as a carcinogen (WANG; LIU; LIU, 2016). BPA and its analogs possess endocrinal activities in humans (GRAMEC SKLEDAR; PETERLIN MAŠIČ, 2016; MALLOZZI et al., 2017).

Another environmental issue of bis-benzoxazine synthesis is its production which mostly requires solvents to avoid some technical limitations. The reaction mixture of a solvent-free bis-benzoxazine synthesis is generally highly viscous, containing chemical species with high melting points with some miscibility problems. And most of the solvents used reported in the literature are highly toxic and inflammable, such as toluene, dioxane, and xylene (CHIU et al., 2016; SAINI; AZECHI; ENDO, 2015). Using these solvents with long-lasting reaction times of hours or days under conventional heating, contributing to more CO_2 release in the atmosphere, turns bis-benzoxazine synthesis barely sustainable.

Green Chemistry and Benzoxazine Synthesis

In our modern world, "sustainability" has become one of the most commented topics nowadays, as it is made clear that our society and future generations are highly dependent on the environment's well-being. In this way, Paul Anastas and John Warner proposed guidance of how Chemistry can contribute heavily to the sustainable economy by offering the book *Green Chemistry* (ANASTAS; WARNER, 1998), which is composed by its twelve principles:

1. *Prevent Waste:* waste prevention is better than treating or cleaning up waste after it has been created;
2. *Atom Economy:* The syntheses must be designed that all the materials used during the process should be introduced as much as possible into the product;
3. *Less Hazardous Synthesis:* when applicable, the synthesis must be designed to use and generate substances with little or no toxicity to the environment and human life.
4. *Design Benign Chemicals:* Chemical products should be designed to affect their desired function while minimizing their toxicity.
5. *Benign Solvents and Auxiliaries*: The use of auxiliaries should be considered unnecessary when possible or use innocuous ones.
6. *Design for Energy Efficiency*: The energy used for a chemical process should be as minimum, efficient, and sustainable as possible. Wherever applicable, reactions under room temperature and pressure are preferred.
7. *The use of renewable feedstocks*: The raw materials used should be renewable and not depleted when technically and economically feasible.
8. *Reduce Derivatives:* Minimize or avoid using derivations (the use of blocking groups, protection/deprotection) as they produce more waste.
9. *Catalysis:* Catalytic reagents are superior to stoichiometric reagents.
10. *Design for degradation:* The chemical product should be designed that when it comes to its end-life, the product must break down, and the remained substances must be innocuous as possible.
11. *Real-time analysis of pollution prevention:* Analytical methodologies need to be further developed to allow for real-time, in-process monitoring and control before the formation of hazardous substances.
12. *Inherently Benign Chemistry for Accident Prevention:* Substances and the form of a substance used in a chemical process should be chosen to minimize the potential for chemical accidents, including releases, explosions, and fires.

After understanding these twelve principles, designing a synthesis that includes all these principles is not an easy task. However, using these principles as much as possible will promote more sustainability to the reaction process and/or the product. For benzoxazine synthesis, three principles are more easily applied and will be discussed from here on, which are: a) the use of renewable feedstocks; b) the use of energy-efficient heating sources; and c) the use of neoteric solvents.

The use of renewable feedstocks for bio-based benzoxazines

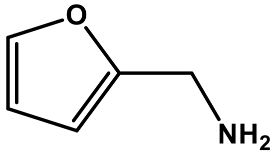
Biomass and biomass-derived materials are essential resources to provide alternative and sustainable chemicals with similar or superior properties to their fossil-based counterparts. Besides being renewable, biomass is widely available around the globe and especially in countries with advanced development in agriculture, such as Brazil, wherein 2016, more than 1.2 billion tons of crops were produced (FAO, 2018). Agriculture biomass is mainly composed of lignocellulose and is an important resource for producing alternative platform chemicals, which are building blocks that can be converted into a wide variety of chemicals or materials (BOMTEMPO; CHAVES ALVES; DE ALMEIDA OROSKI, 2017).

The use of bio-chemicals to produce bio-based benzoxazines has been widely studied by using mainly renewable phenolic compounds such as eugenol (DUMAS et al., 2015), iso-eugenol (SHARMA et al., 2018), vanillin (SINI; BIJWE; VARMA, 2014), guaiacol (RUČIGAJ; GRADIŠAR; KRAJNC, 2016), urushiol (XU et al., 2013) and cardanol (A. ATTANASI et al., 2012; CALÒ et al., 2007; KOTZEBUE et al., 2016). Even though bio-based amines are less available when compared to renewable phenolic compounds, some renewable amines were reported for benzoxazine syntheses, such as stearylamine and furfurylamine (WANG et al., 2012).

Lignocellulose

Lignocellulose is a fibrous material localized in the cell wall of vascular plants, and it is mainly composed of three polymers: cellulose, hemicellulose, and lignin. The major component of lignocellulose is cellulose, a crystalline long polymer chain consisting of *β*-1,4-linked D-glucose units (SHELDON, 2018b). The second most abundant polymer is hemicellulose, an amorphous short polymer chain derived from various C_5 and C_6 sugars, such as D-arabinose, D-xylose, D-glucose, and D-galactose (SHELDON, 2018b). These two carbohydrates are important resources for producing aldehydes, which can be further converted into amines by different chemical processes (HÜLSEY; YANG; YAN, 2018). An example is that cellulose and hemicellulose can produce furfural and furfural derivatives (such as 5-hydroxymethylfurfural), important platform chemicals for the production of renewable primary amines, such as furfurylamine (Figure 11) (ISIKGOR; BECER, 2015; SHELDON, 2018b).

Figure 11 - Molecular structure of furfurylamine

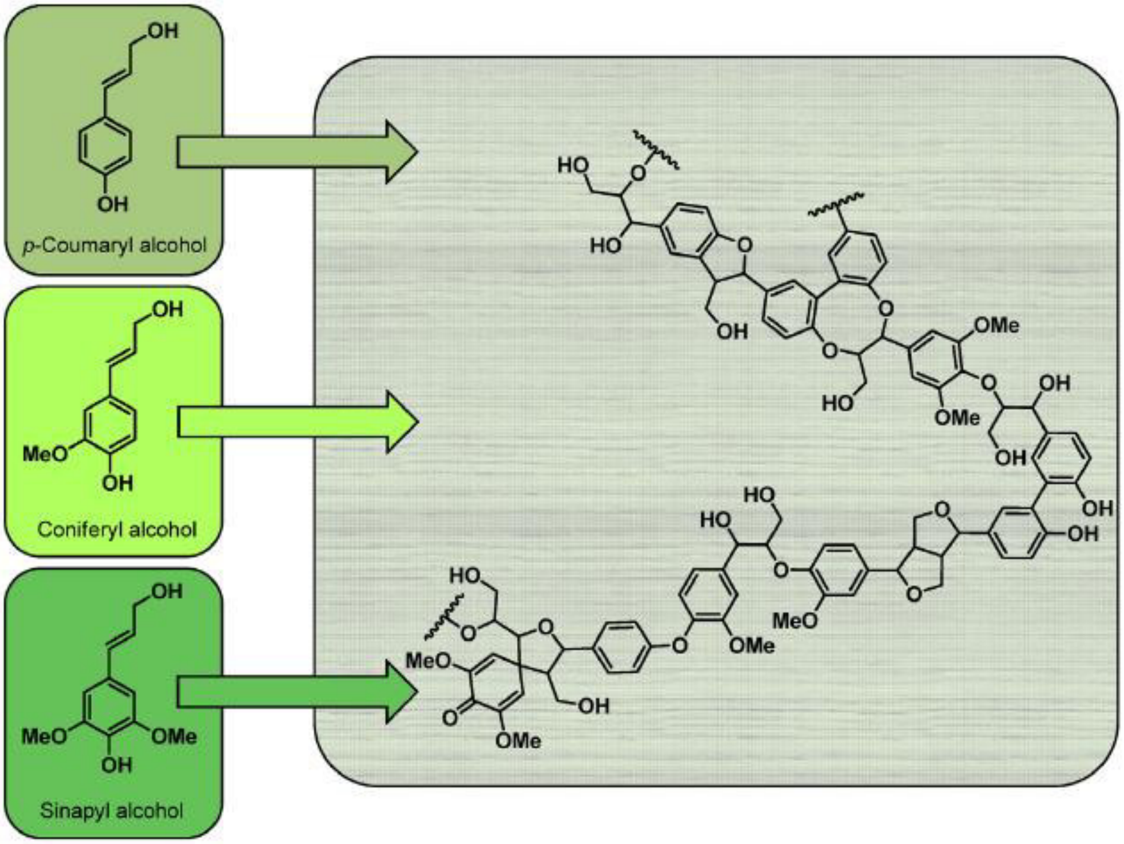


Source: The author

Furfurylamine has been used as an interesting primary amine for benzoxazine synthesis, demonstrating polymers with peculiar characteristics. Benzoxazines containing furfurylamine usually have higher melting points than those containing aniline derivates (KOTZEBUE et al., 2016; OLIVEIRA et al., 2017). When it comes to polybenzoxazines, furfurylamine can improve the thermal properties of the polymer compared to aniline-based polybenzoxazines. As the glass transition temperatures of the aniline-based polybenzoxazine **P-BPA-ABz** was 171 °C, the furfurylamine-based polybenzoxazine **P-BPA-FBz** had an impressive glass transition temperature of 308 °C (LIU; CHOU, 2005). Analyzing the char yield of both polybenzoxazines, it was observed that the char yield of **P-BPA-FBz** was 17 % higher than **P-BPA-ABz** (LIU; CHOU, 2005). The high thermal properties of furfurylamine-based polybenzoxazines were also reported elsewhere (DAI et al., 2018; DUMAS et al., 2016b), and the reason for this is due to the reactive α-carbon of the furfuryl group, favoring the formation of higher crosslink densities in the polymer matrix (FROIMOWICZ et al., 2016). Therefore, besides being renewable, furfurylamine is highly suitable as a primary amine to produce high-performance bio-based polybenzoxazines.

The third most abundant component of lignocellulose is lignin, a highly branched and amorphous macromolecule biosynthesized after radical polymerization of methoxylated hydroxycinnamyl alcohols, such as coniferyl alcohol, p-coumaryl alcohol, and sinapyl alcohol (Figure 12) (AHMAD; SILVA; VARESCHE, 2018; ZIRBES; WALDVOGEL, 2018).

Figure 12 - Representative of the structure of lignin and its building blocks



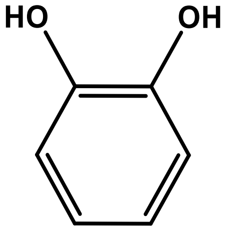
Source: ZIRBES; WALDVOGEL, 2018

Lignin is the largest sustainable feedstock renewable of phenolic compounds and is produced annually from 40 to 60 million tons as a waste product (MOVIL-CABRERA et al., 2016). As it is highly resistant to external stresses and protects the inner parts of plant cells, lignin possesses a chemical structure that makes it not easy to degrade, making it more useful as fuel for the pulp industry (WENDISCH; KIM; LEE, 2018). However, much research has been done to study the depolymerization of lignin into value-added products, such as vanillin. Synthetic vanillin is obtained from lignin, representing 90 % of the annual 20,000 tons market. Other value-added aromatic compounds are yet to be introduced into the market, such as phenolic aldehydes and phenolics (WENDISCH; KIM; LEE, 2018).

Although the complex heterogeneity of the lignin structure, by using biotechnological (BECKHAM et al., 2016), electrochemical (MOVIL-CABRERA et al., 2016; ZIRBES; WALDVOGEL, 2018), thermal (NAIR; VINU, 2016), hydrothermal processes (ZHANG et al., 2014), many other value-added lignin-based aromatics can be produced such as guaiacol (NAIR; VINU, 2016), cresol (WAHYUDIONO; SASAKI; GOTO, 2008) and catechol (JEENPADIPHAT; MONGKOLPICHAYARAK; TUNGASMITA, 2016; WAHYUDIONO; SASAKI; GOTO, 2008).

Catechol, also known as 1,2-dihydroxybenzene (Figure 13), is an interesting phenolic compound to obtain bio-based bis-benzoxazine, and no study on its synthesis has been reported. Dumas and co-workers developed bis-benzoxazine from resorcinol and hydroquinone, analogs of catechol, demonstrating polybenzoxazines with high thermomechanical properties (DUMAS et al., 2016b). It is believed that catechol can act as a promising starting material for developing renewable high-performance polybenzoxazines.

Figure 13 - Molecular Structure of Catechol

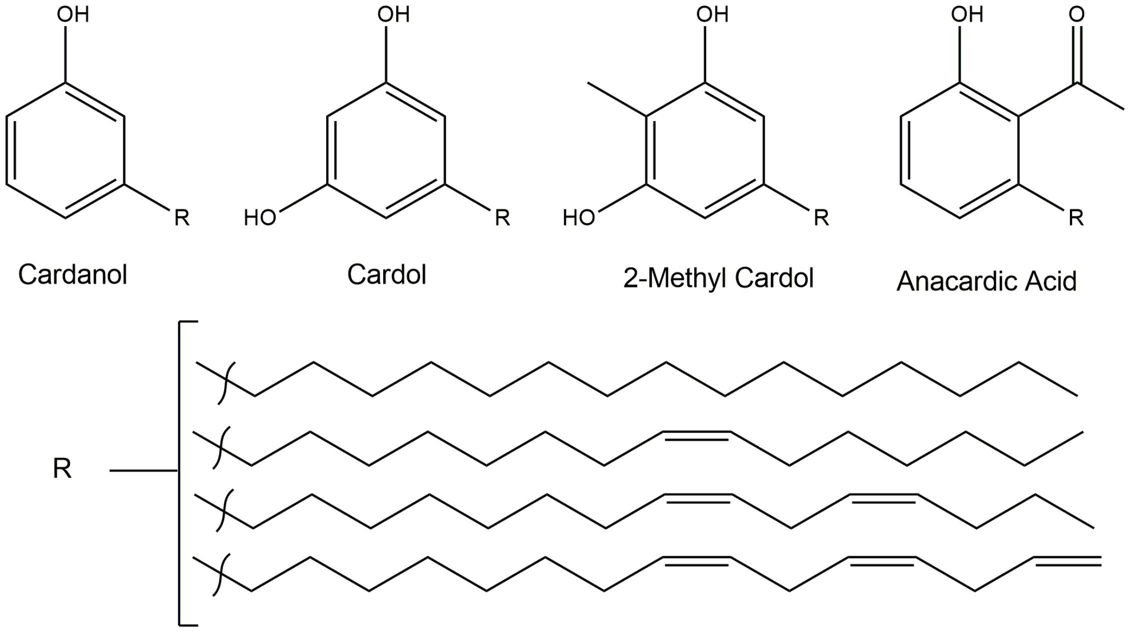


Source: The author

Cashew Nut Shell Liquid

After lignin, another potential renewable resource rich in phenolic compounds is Cashew Nut Shell Liquid (CNSL), the main by-product of the cashew nut almond industries. Found in the spongy mesocarp of the cashew nut shell (*Anacardium Occidentalle L.*), CNSL is a dark brown viscous caustic liquid, and it is composed of long aliphatic chain (C_{15}) phenolics. The chemical composition is mainly of anacardic acid, cardanol, cardol, and 2-methyl cardol (Figure 14) (MAZZETTO; LOMONACO, 2009), where the concentration of each phenolic depends on its origin and the treatment suffered (Table 1). Natural CNSL possesses a high concentration of anacardic acid, and due to the high thermal processing to obtain the valuable cashew nut almond, the anacardic acid of natural CNSL suffers a decarboxylation reaction, turning the CNSL rich in cardanol, which is now called as “technical CNSL” (LOMONACO; MELE; MAZZETTO, 2017).

Figure 14 - Molecular structures of the chemical composition of CNSL



Source: The author

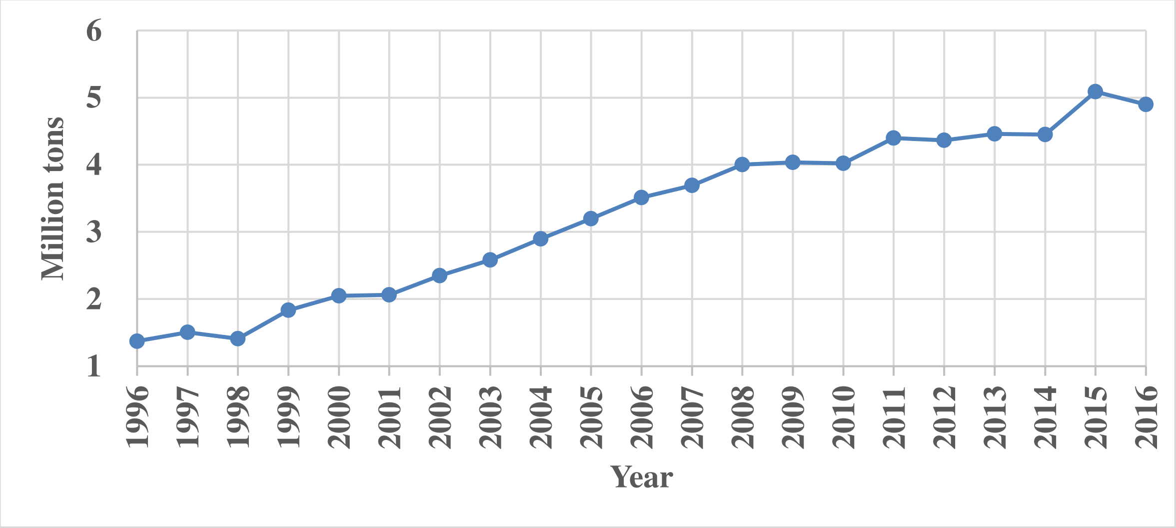
Table 1 - Chemical composition of natural and technical CNSL

Phenolic compounds	Natural (%)	Technical (%)
Anacardic acid	71.70 – 82.00	1.09 – 1.75
Cardanol	1.60 – 9.20	67.82 – 94.60
Cardol	13.80 – 20.10	3.80 – 18.86
2-methyl cardol	1.65 – 3.90	1.20 – 4.10
Minor components	2.20	3.05 – 3.98
Polymeric materials	---	0.34 – 21.63

Source: MAZZETTO; LOMONACO, 2009

The world production of cashew nuts with shell has shown, in general, a growing annual tendency (Figure 15) (FAO, 2018). Considering that in 2015 the world production was more than 5 million tons and knowing that CNSL represents 25 % in weight of the cashew nut with shell, it is estimated that 1.25 million tons of this by-product could be produced. This huge amount of renewable starting materials is very promising to produce bio-based materials in large quantities. This feedstock is low-cost and already used compared to lignin-based phenolics obtained after using complicated processes, as cited earlier.

Figure 15 - World Production of Cashew Nut (with Shell)

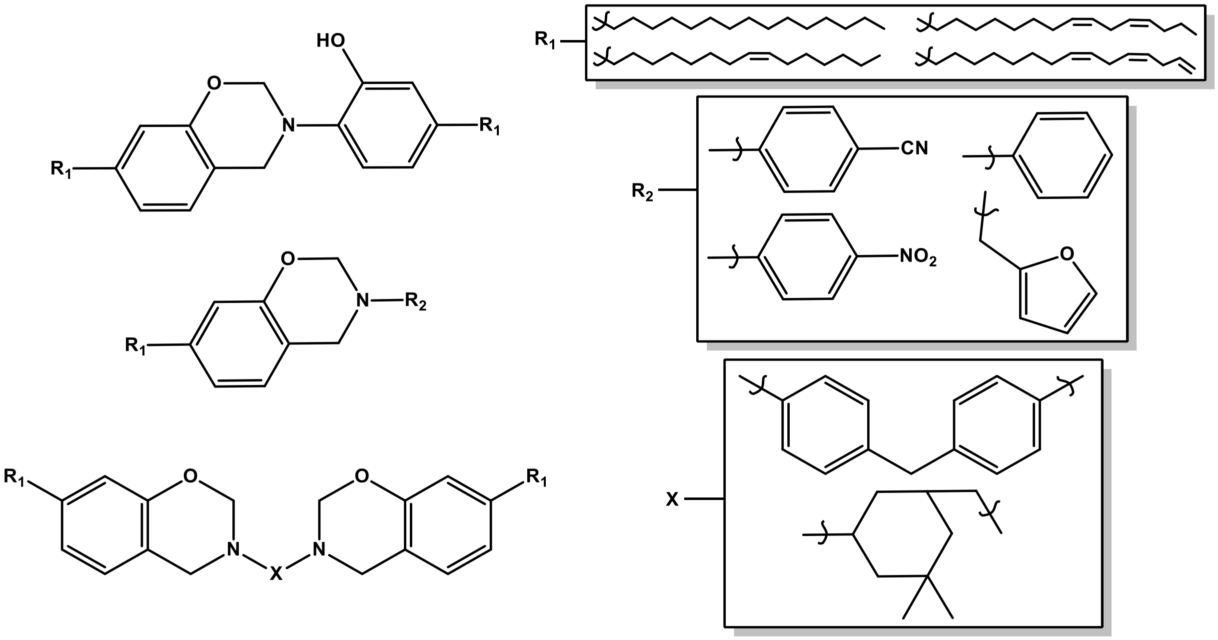


Source: FAO, 2018

In 2007, the synthesis of the first cardanol-based benzoxazine was reported, which used ammonia as an amine source (CALÒ et al., 2007). After that, many other cardanol-based (mono- and bis-) benzoxazines were synthesized with a variety of primary amines (Figure 16) (A. ATTANASI et al., 2012; LOCHAB; VARMA; BIJWE, 2010, 2011).

Unfortunately, cardanol-based polybenzoxazines are not ideal for high-performance materials due to their low thermal and mechanical properties. Even though cardanol-based polybenzoxazines possess initial degradation temperatures that reach 398 °C, they usually have low char yields (LOCHAB; VARMA; BIJWE, 2010, 2011), especially low glass transition temperatures. For example, Calò and co-workers' mono-benzoxazine, containing two cardanol groups, offered a polymer with a T_g of 36 °C (CALÒ et al., 2007). Ambrožič and coworkers reported higher glass transition temperatures for their cardanol-based polybenzoxazines. However, they were still not ideal for high-performance materials. Their monofunctional cardanol-benzoxazines had T_g of 89 and 99 °C. by using aniline and furfurylamine, respectively (AMBROŽIČ; ŠEBENIK; KRAJNC, 2015). To increase crosslinking, other attempts were made to provide higher crosslink densities by synthesizing bifunctional or epoxidized cardanol-based benzoxazine. However, the T_g*'s* of their polymers ranged from 106 to 110 °C (AMBROŽIČ; ŠEBENIK; KRAJNC, 2015). This low glass transition temperature of cardanol-based polybenzoxazine is mainly due to the large number of aliphatic chains present in the polymer matrix, which lowers the crosslink densities.

Figure 16 - Some examples of reported cardanol-based benzoxazines



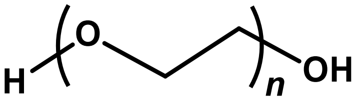
Source: The author

Poly(ethylene glycol) as "green" solvent and microwave-heating for bis-benzoxazine synthesis

As described earlier that the use of solvents for bis-benzoxazine synthesis is a necessity, neoteric solvents can fulfill this role. When it comes to neoteric solvents, ionic liquids and supercritical fluids are more known to be more benign than toxic fossil-based ones (SHELDON, 2017). Still, there is another one that is gaining attention which is poly(ethylene glycol).

Poly(ethylene glycol), also known as PEG (Figure 12), is a commercially available polyether with a variety of polymer chain lengths that can be used from pharmaceutical to coating applications (BRADY et al., 2017), and for being non-toxic, it has been approved by the U.S. Food and Drug Administration (FDA) for internal consumption (HARRIS, 1992).

Figure 17 - Chemical structure of PEG



Source: The Author

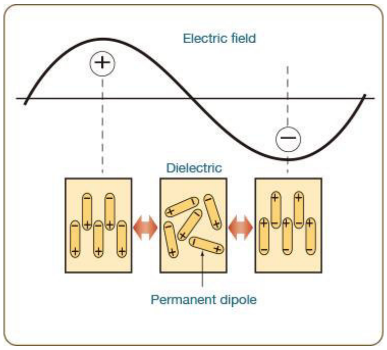
The use of PEG for benzoxazine synthesis has already been reported to be used as a reactant (BROWN; RIDER, 2017; TREJO-MACHIN et al., 2017), but not as a result safe and inactive solvent. PEG is an interesting alternative to the conventional organic solvents due to its peculiar properties (CHEN et al., 2005; VAFAEEZADEH; HASHEMI, 2015), such as:

- High chemical stability in acidic and basic media and at high temperatures;
- Wide solvent miscibility, from protic to non-polar solvents;
- Immiscible with aliphatic hydrocarbons;
- Can be recovered by extraction or direct distillation;
- It is biodegradable and non-volatile;
- Possess low flammability.

Another interesting ability of PEG is its capability to absorb microwave-irradiation, which is useful for microwave dielectric heating (CINI; PETRICCI; TADDEI, 2017; DRIOWYA et al., 2016).

Microwave-assisted organic synthesis (MAOS) is an alternative synthetic method that uses microwave irradiation as a heating source. Certain reactants, usually molecules containing molecular dipoles or charges, can absorb microwave energy and convert it into heat, also known as microwave dielectric heating. At a frequency of 2.45 GHz, the electric field of the electromagnetic wave causes heating by two main mechanisms (KAPPE, 2004): a) ionic conduction and; b) dipolar polarization. Due to the oscillating electric component of the electromagnetic field, microwave active species (dipoles and ions) attempts to align and realign with the alternating electric field (Figure 18), which causes heat by molecular friction and dielectric losses (KAPPE, 2004).

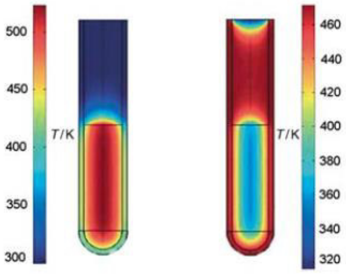
Figure 18 - Electric field and movement of molecules in a Dielectric



Source: VINITA, 2018

Understanding the heating mechanism clarifies that microwave irradiation has an efficient internal heat transfer, which is contrary to the long-lasting traditional heat transfer that comes from the vessel's wall to the reactants (Figure 19). Besides better energy efficiency, MAOS has other advantages like short reaction time, high reaction yields, higher product purity, and low by-product generation

Figure 19 - Inverted temperature gradients of microwave (left) and oil-bath heating (right)



Source: KAPPE, 2004

REFERENCES

A. ATTANASI, O. et al. Solvent Free Synthesis of Novel Mono- and Bis-Benzoxazines from Cashew Nut Shell Liquid Components. **Current Organic Chemistry**, v. 16, n. 21, p. 2613–2621, 2012.

AGAG, T.; JIN, L.; ISHIDA, H. A new synthetic approach for difficult benzoxazines: Preparation and polymerization of 4,4′-diaminodiphenyl sulfone-based benzoxazine monomer. **Polymer**, v. 50, n. 25, p. 5940–5944, 2009.

AHMAD, F.; SILVA, E. L.; VARESCHE, M. B. A. Hydrothermal processing of biomass for anaerobic digestion – A review. **Renewable and Sustainable Energy Reviews**, v. 98, n. December 2017, p. 108–124, 2018.

ALTIN KARATAŞ, M.; GÖKKAYA, H. A review on machinability of carbon fiber reinforced polymer (CFRP) and glass fiber reinforced polymer (GFRP) composite materials. **Defence Technology**, v. 14, n. 4, p. 318–326, ago. 2018.

AMARNATH, N.; APPAVOO, D.; LOCHAB, B. Eco-Friendly Halogen-Free Flame Retardant Cardanol Polyphosphazene Polybenzoxazine Networks. **ACS Sustainable Chemistry & Engineering**, v. 6, n. 1, p. 389–402, 2 jan. 2018.

AMBROŽIČ, R.; ŠEBENIK, U.; KRAJNC, M. Synthesis, curing kinetics, thermal and mechanical behavior of novel cardanol-based benzoxazines. **Polymer**, v. 76, p. 203–212, out. 2015.

ANASTAS, P. T.; WARNER, J. C. **Green Chemistry: Theory and Practice**. New York: Oxford University Press, 1998.

BARANEK, A. D. et al. Flexible aliphatic-bridged bisphenol-based polybenzoxazines. **Polymer Chemistry**, v. 3, n. 10, p. 2892–2900, 2012.

BECKHAM, G. T. et al. Opportunities and challenges in biological lignin valorization. **Current Opinion in Biotechnology**, v. 42, n. March, p. 40–53, dez. 2016.

BERESKA, A. et al. The application of organophosphorus flame-retardants in epoxy resin. **Journal of Vinyl and Additive Technology**, v. 23, n. 2, p. 142–151, maio 2017.

BILAL, M. et al. Biotransformation of lignocellulosic materials into value-added products—A review. **International Journal of Biological Macromolecules**, v. 98, p. 447–458, 2017.

BOBADE, S. K. et al. Bio-Based Thermosetting Resins for Future Generation: A Review. **Polymer-Plastics Technology and Engineering**, v. 55, n. 17, p. 1863–1896, 2016.

BOMTEMPO, J.-V.; CHAVES ALVES, F.; DE ALMEIDA OROSKI, F. Developing new platform chemicals: what is required for a new bio-based molecule to become a platform

chemical in the bioeconomy? **Faraday Discuss.**, v. 202, p. 213–225, 2017.

BRADY, J. et al. Developing Solid Oral Dosage Forms. In: QIU, Y. et al. (Eds.). . 2nd. ed. [s.l.] Academic Press, 2017. p. 1176.

BROWN, E. A.; RIDER, D. A. Pegylated Polybenzoxazine Networks with Increased Thermal Stability from Miscible Blends of Tosylated Poly(ethylene glycol) and a Benzoxazine Monomer. **Macromolecules**, v. 50, n. 17, p. 6468–6481, 2017.

BURKE, W. J. 3,4-Dihydro-1,3,2H-Benzoxazines. Reaction of p -Substituted Phenols with N,N-Dimethylolamines. **Journal of the American Chemical Society**, v. 71, n. 2, p. 609–612, 1949.

BURKE, W. J. et al. A New Aminoalkylation Reaction. Condensation of Phenols with Dihydro-1,3-aroxazines. **The Journal of Organic Chemistry**, v. 30, n. 10, p. 3423–3427, 1965.

BURKE, W. J.; GLENNIE, E. L. M.; WEATHERBEE, C. Condensation of Halophenols with Formaldehyde and Primary Amines. **The Journal of Organic Chemistry**, v. 29, n. 4, p. 909–912, 1964.

BURKE, W. J.; MURDOCK, K. C.; EC, G. Condensation of Hydroxyaromatic Compounds with Formaldehyde and Primary Aromatic Amines. **Journal of the American Chemical Society**, v. 76, n. 6, p. 1677–1679, 1954.

BURKE, W. J.; SMITH, R. P.; WEATHERBEE, C. N,N-Bis-(hydroxybenzyl)-amines: Synthesis from Phenols, Formaldehyde and Primary Amines. **Journal of the American Chemical Society**, v. 74, n. 3, p. 602–605, 1952.

BURKE, W. J.; STEPHENS, C. W. Monomeric Products from the Condensation of Phenol with Formaldehyde and Primary Amines. **Journal of the American Chemical Society**, v. 74, n. 6, p. 1518–1520, mar. 1952.

BURKE, W. J.; WEATHERBEE, C. 3,4-Dihydro-1,3,2H-Benzoxazines. Reaction of Polyhydroxybenzenes with N-Methylolamines 1. **Journal of the American Chemical Society**, v. 72, n. 10, p. 4691–4694, out. 1950.

CALÒ, E. et al. Synthesis of a novel cardanol-based benzoxazine monomer and environmentally sustainable production of polymers and bio-composites. **Green Chemistry**, v. 9, n. 7, p. 754–759, 2007.

CHEN, J. et al. Polyethylene glycol and solutions of polyethylene glycol as green reaction media. **Green Chemistry**, v. 7, n. 2, p. 64–82, 2005.

CHEN, Z.; WAN, C. Biological valorization strategies for converting lignin into fuels and chemicals. **Renewable and Sustainable Energy Reviews**, v. 73, p. 610–621, jun. 2017.

CHIU, W.-M. et al. Preparation and characterization of novel polybenzoxazine hybrid materials. **High Performance Polymers**, v. 28, n. 8, p. 971–983, 2016.

CHOI, S.-W. et al. Synthesis, characterization and thermal degradation of functional benzoxazine monomers and polymers containing phenylphosphine oxide. **Polymer Degradation and Stability**, v. 91, n. 5, p. 1166–1178, maio 2006.

CINI, E.; PETRICCI, E.; TADDEI, M. Pd/C Catalysis under Microwave Dielectric Heating. **Catalysts**, v. 7, n. 12, p. 89, 20 mar. 2017.

DAI, J. et al. Biobased Benzoxazine Derived from Daidzein and Furfurylamine: Microwave-Assisted Synthesis and Thermal Properties Investigation. **ChemSusChem**, v. 11, n. 18, p. 3175–3183, 21 set. 2018.

DAYO, A. Q. et al. Natural hemp fiber reinforced polybenzoxazine composites: Curing behavior, mechanical and thermal properties. **Composites Science and Technology**, v. 144, p. 114–124, maio 2017.

DE LEON, A. C. et al. High performance polymer nanocomposites for additive manufacturing applications. **Reactive and Functional Polymers**, v. 103, p. 141–155, jun. 2016.

DENG, C. et al. Modes of action of a mono-component intumescent flame retardant MAPP in polyethylene-octene elastomer. **Polymer Degradation and Stability**, v. 138, p. 142–150, 2017.

DHOLAKIYA, B. Unsaturated Polyester Resin for Specialty Applications. In: SALEH, H. E.-D. M. (Ed.). . **Polyester**. Rijeka: InTech, 2012. p. 432.

DOUSE, E. et al. Modification of stress-strain behaviour in aromatic polybenzoxazines using core shell rubbers. **Reactive and Functional Polymers**, v. 103, p. 117–130, jun. 2016.

DRIOWYA, M. et al. **Microwave-assisted synthesis of bioactive six-membered heterocycles and their fused analogues**. [s.l: s.n.]. v. 21

DUMAS, L. et al. Eugenol-based benzoxazine: from straight synthesis to taming of the network properties. **J. Mater. Chem. A**, v. 3, n. 11, p. 6012–6018, 2015.

DUMAS, L. et al. Arbutin-based benzoxazine: en route to an intrinsic water soluble biobased resin. **Green Chem.**, v. 18, n. 18, p. 4954–4960, 2016a.

DUMAS, L. et al. High performance bio-based benzoxazine networks from resorcinol and hydroquinone. **European Polymer Journal**, v. 75, p. 486–494, fev. 2016b.

DUMAS, L. et al. Chavicol benzoxazine: Ultrahigh Tg biobased thermoset with tunable extended network. **European Polymer Journal**, v. 81, p. 337–346, ago. 2016c.

ERDOCIA, X. et al. Base catalyzed depolymerization of lignin: Influence of organosolv lignin nature. **Biomass and Bioenergy**, v. 66, p. 379–386, jul. 2014.

FANG, Y. et al. Flame retardant performance of a carbon source containing DOPO derivative in PET and epoxy. **Journal of Applied Polymer Science**, v. 134, n. 12, p. 1–9, 2017.

FAO. **FAO**. Disponível em: http://faostat3.fao.org/faostat-gateway/go/to/browse/Q/QC/E. Acesso em: 28 set. 2018.

FERNÁNDEZ-RODRÍGUEZ, J. et al. Lignin depolymerization for phenolic monomers production by sustainable processes. **Journal of Energy Chemistry**, v. 26, n. 4, p. 622–631, jul. 2017.

FROIMOWICZ, P. et al. Smart, Sustainable, and Ecofriendly Chemical Design of Fully Bio-Based Thermally Stable Thermosets Based on Benzoxazine Chemistry. **ChemSusChem**, v. 9, n. 15, p. 1921–1928, 2016.

FROIMOWICZ, P.; ZHANG, K.; ISHIDA, H. Intramolecular Hydrogen Bonding in Benzoxazines: When Structural Design Becomes Functional. **Chemistry - A European Journal**, v. 22, n. 8, p. 2691–2707, 2016.

FU, T. et al. Inherent flame retardation of semi-aromatic polyesters via binding small-molecule free radicals and charring. **Polymer Chemistry**, v. 7, n. 8, p. 1584–1592, 2016.

GAO, Y. et al. Unsaturated polyester resin concrete: A review. **Construction and Building Materials**, v. 228, p. 116709, 2019.

GRAMEC SKLEDAR, D.; PETERLIN MAŠIČ, L. Bisphenol A and its analogs: Do their metabolites have endocrine activity? **Environmental Toxicology and Pharmacology**, v. 47, p. 182–199, 2016.

HAN, L. et al. Oxazine Ring-Related Vibrational Modes of Benzoxazine Monomers Using Fully Aromatically Substituted, Deuterated, 15 N Isotope Exchanged, and Oxazine-Ring-Substituted Compounds and Theoretical Calculations. **The Journal of Physical Chemistry A**, v. 121, n. 33, p. 6269–6282, 2017.

HARRIS, J. M. (ED.). Poly(Ethylene Glycol) Chemistry. In: **Biotechnical and Biomedical Applications**. Boston, MA: Springer US, 1992.

HASSAN, W. A. W. et al. Examining the influence of bisphenol A on the polymerisation and network properties of an aromatic benzoxazine. **Polymer**, v. 88, p. 52–62, 2016.

HILL, D. J. T. et al. Dynamic mechanical properties of networks prepared from siloxane modified divinyl benzene pre-polymers. **Polymer**, v. 41, n. 26, p. 9131–9137, dez. 2000.

HOLLY, F. W.; COPE, A. C. Condensation Products of Aldehydes and Ketones with o-Aminobenzyl Alcohol and o-Hydroxybenzylamine. **Journal of the American Chemical Society**, v. 66, n. 11, p. 1875–1879, nov. 1944.

HÜLSEY, M. J.; YANG, H.; YAN, N. Sustainable Routes for the Synthesis of Renewable Heteroatom-Containing Chemicals. **ACS Sustainable Chemistry & Engineering**, v. 6, n. 5, p. 5694–5707, 7 maio 2018.

HUNTSMAN. **Benzoxazines**. Disponível em: http://www.huntsman.com/advanced_materials/a/Our Technologies/High Performance Components/Imides and Benzoxazines/Benzoxazines. Acesso em: 22 set. 2018.

IREDALE, R. J.; WARD, C.; HAMERTON, I. Modern advances in bismaleimide resin technology: A 21st century perspective on the chemistry of addition polyimides. **Progress in Polymer Science**, v. 69, p. 1–21, jun. 2017.

ISHIDA, H.; AGAG, T. Handbook of Benzoxazine Resins. In: ISHIDA, H.; AGAG, T. (Eds.). . **Handbook of Benzoxazine Resins**. Oxford: Elsevier, 2011. p. 712.

ISHIDA, H.; SANDERS, D. P. Improved Thermal and Mechanical Properties of Polybenzoxazines Based on Alkyl-Substituted Aromatic Amines. **Polymer**, v. 38, p. 3289–3301, 2000.

ISIKGOR, F. H.; BECER, C. R. Lignocellulosic biomass: a sustainable platform for the production of bio-based chemicals and polymers. **Polymer Chemistry**, v. 6, n. 25, p. 4497–4559, 2015.

JEENPADIPHAT, S.; MONGKOLPICHAYARAK, I.; TUNGASMITA, D. N. Catechol production from lignin by Al-doped mesoporous silica catalytic cracking. **Journal of Analytical and Applied Pyrolysis**, v. 121, p. 318–328, set. 2016.

KALIAVARADHAN, K.; MUTHUSAMY, S. Synthesis and characterization of various phenylene diamine-based bismaleimide-containing phthalonitrile resins. **Polymer Bulletin**, v. 73, n. 7, p. 1921–1938, 2016.

KAPPE, C. O. Controlled Microwave Heating in Modern Organic Synthesis. **Angewandte Chemie International Edition**, v. 43, n. 46, p. 6250–6284, 26 nov. 2004.

KATHALEWAR, M.; SABNIS, A.; D'MELO, D. Polyurethane coatings prepared from CNSL based polyols: Synthesis, characterization and properties. **Progress in Organic Coatings**, v. 77, n. 3, p. 616–626, 2014.

KHAN, M. A. et al. Experimental and numerical analysis of flexural and impact behaviour of glass/pp sandwich panel for automotive structural applications. **Advanced Composite Materials**, v. 27, n. 4, p. 367–386, 4 jul. 2018.

KISKAN, B. Adapting benzoxazine chemistry for unconventional applications. **Reactive and Functional Polymers**, v. 129, p. 76–88, ago. 2018.

KOPSIDAS, S.; HAMERTON, I. Examining the thermal behaviour of novel aromatic polybenzoxazine blends containing an organophosphorous compound and polyhedral oligomeric silsesquioxane reagents. **Polymer International**, v. 65, n. 9, p. 1015–1023, set. 2016.

KOTZEBUE, L. R. V. et al. Spectral and thermal studies on the synthesis and catalyzed oligomerization of novel cardanol-based benzoxazines. **Polymer**, v. 92, p. 189–200, 2016.

KOTZEBUE, L. R. V. et al. Development of Fully Biobased High-Performance Bis-Benzoxazine under Environmentally Friendly Conditions. **ACS Sustainable Chemistry & Engineering**, v. 6, n. 4, p. 5485–5494, 2018.

LAURICHESSE, S.; AVÉROUS, L. Chemical modification of lignins: Towards biobased polymers. **Progress in Polymer Science**, v. 39, n. 7, p. 1266–1290, 2014.

LI, B. et al. Preparation of bio-based phenol formaldehyde foams using depolymerized hydrolysis lignin. **Industrial Crops and Products**, v. 97, p. 409–416, mar. 2017.

LI, W. et al. Preparation of novel benzoxazine monomers containing ferrocene moiety and properties of polybenzoxazines. **Polymer**, v. 53, n. 6, p. 1236–1244, 2012.

LIN, C. H. et al. Synthesis of a Bisbenzylideneacetone-Containing Benzoxazine and Its Photo- and Thermally Cured Thermoset. **ACS Omega**, v. 2, n. 7, p. 3432–3440, 2017.

LIU, Y.-L.; CHOU, C.-I. High performance benzoxazine monomers and polymers containing furan groups. **Journal of Polymer Science Part A: Polymer Chemistry**, v. 43, n. 21, p. 5267–5282, 2005.

LLIGADAS, G. et al. Polybenzoxazines: new players in the bio-based polymer arena. **Polym. Chem.**, v. 5, n. 23, p. 6636–6644, 2014.

LOCHAB, B.; VARMA, I. K.; BIJWE, J. Thermal behaviour of cardanol-based benzoxazines. **Journal of Thermal Analysis and Calorimetry**, v. 102, n. 2, p. 769–774, 9 nov. 2010.

LOCHAB, B.; VARMA, I. K.; BIJWE, J. Cardanol-based bisbenzoxazines. **Journal of Thermal Analysis and Calorimetry**, v. 107, n. 2, p. 661–668, 26 ago. 2011.

LOMONACO, D. et al. Thermal studies of new biodiesel antioxidants synthesized from a natural occurring phenolic lipid. **Fuel**, v. 97, p. 552–559, jul. 2012.

LOMONACO, D.; MELE, G.; MAZZETTO, S. E. Cashew Nutshell Liquid (CNSL): From an Agro-industrial Waste to a Sustainable Alternative to Petrochemical Resources. In: ANILKUMAR, P. (Ed.). . **Cashew Nut Shell Liquid**. Zurich: Springer, Cham, 2017. p. 19–38.

LYU, Y.; ISHIDA, H. Natural-sourced benzoxazine resins, homopolymers, blends and composites: A review of their synthesis, manufacturing and applications. **Progress in Polymer Science**, v. 99, p. 101168, dez. 2019.

MA, R.; GUO, M.; ZHANG, X. Recent advances in oxidative valorization of lignin. **Catalysis Today**, v. 302, p. 50–60, 2018.

MALLAKPOUR, S.; ZADEHNAZARI, A. Improved covalent functionalization of multi-walled carbon nanotubes using ascorbic acid for poly(amide–imide) composites having dopamine linkages. **Bulletin of Materials Science**, v. 40, n. 1, p. 213–222, 2017.

MALLOZZI, M. et al. Endocrine Disrupting Chemicals and Endometrial Cancer: An Overview of Recent Laboratory Evidence and Epidemiological Studies. **International Journal of Environmental Research and Public Health**, v. 14, n. 3, p. 334, 2017.

MAMANPUSH, S. H. et al. Recycled wind turbine blades as a feedstock for second generation composites. **Waste Management**, v. 76, p. 708–714, jun. 2018.

MANIKANNAN, R.; MUTHUSUBRAMANIAN, S. Synthesis and biological activity of 6-alkyl/chloro-3-{4-(6-alkyl/chloro-2H-benzo[e][1,3]oxazin-3(4H)-yl}-3,4-dihydro-2H-benzo[e][1,3]oxazines. **Indian Journal of Chemistry**, v. 49B, n. August, p. 1083–1087, 2010.

MARTINEZ, C. R.; IVERSON, B. L. Rethinking the term “pi-stacking”. **Chemical Science**, v. 3, n. 7, p. 2191–2201, 2012.

MAZZETTO, S. E.; LOMONACO, D. Cashew nut oil: opportunities and challenges in the context of sustainable industrial. **Quimica Nova**, v. 32, n. 3, p. 732–741, 2009.

MENARD, K. P. DYNAMIC MECHANICAL ANALYSIS - A Practical Introduction. In: Boca Raton: CRC Press, 1999. p. 240.

MONISHA, M. et al. Cardanol Benzoxazines: A Versatile Monomer with Advancing Applications. **Macromolecular Chemistry and Physics**, v. 220, n. 3, p. 1800470, 11 fev. 2019.

MOVIL-CABRERA, O. et al. Electrochemical conversion of lignin to useful chemicals. **Biomass and Bioenergy**, v. 88, p. 89–96, maio 2016.

NAIR, C. Advances in addition-cure phenolic resins. **Progress in Polymer Science**, v. 29, n. 5, p. 401–498, maio 2004.

NAIR, V.; VINU, R. Production of guaiacols via catalytic fast pyrolysis of alkali lignin using titania, zirconia and ceria. **Journal of Analytical and Applied Pyrolysis**, v. 119, p. 31–39, maio 2016.

NATARAJAN, M.; MURUGAVEL, S. C. Synthesis, spectral and thermal degradation kinetics of novolac resins derived from cardanol. **High Performance Polymers**, v. 25, n. 6, p. 685–696, 2013.

NG, F. et al. Bio-Based Aromatic Epoxy Monomers for Thermoset Materials. **Molecules**, v. 22, n. 1, p. 149, 18 jan. 2017.

NIELSEN, L. E. Cross-Linking–Effect on Physical Properties of Polymers. **Journal of Macromolecular Science, Part C**, v. 3, n. 1, p. 69–103, 10 jan. 1969.

NING, X.; ISHIDA, H. Phenolic materials via ring-opening polymerization of benzoxazines: Effect of molecular structure on mechanical and dynamic mechanical properties. **Journal of Polymer Science Part B: Polymer Physics**, v. 32, n. 5, p. 921–927, 15 abr. 1994a.

NING, X.; ISHIDA, H. Phenolic materials via ring-opening polymerization: Synthesis and characterization of bisphenol-A based benzoxazines and their polymers. **Journal of Polymer Science Part A: Polymer Chemistry**, v. 32, n. 6, p. 1121–1129, 30 abr. 1994b.

ODIAN, G. **Principles of Polymerization**. 4th. ed. New Jersey: Wiley-Interscience, 2004.

OLIVEIRA, J. R. et al. Microwave-assisted solvent-free synthesis of novel benzoxazines: A faster and environmentally friendly route to the development of bio-based thermosetting resins. **Journal of Polymer Science Part A: Polymer Chemistry**, v. 55, n. 21, p. 3534–3544, 1 nov. 2017.

PERIYASAMY, T.; ASRAFALI, S. P.; KIM, S.-C. Functionalized MWCNTs, an efficient reinforcement for the preparation of eugenol based high performance PBz/BMI/CNT nanocomposites exhibiting outstanding thermo-mechanical properties. **New Journal of Chemistry**, v. 41, n. 14, p. 6607–6615, 2017.

PHALAK, G. A.; PATIL, D. M.; MHASKE, S. T. Synthesis and characterization of thermally curable guaiacol based poly(benzoxazine-urethane) coating for corrosion protection on mild steel. **European Polymer Journal**, v. 88, p. 93–108, mar. 2017.

RAQUEZ, J.-M. et al. Thermosetting (bio)materials derived from renewable resources: A critical review. **Progress in Polymer Science**, v. 35, n. 4, p. 487–509, abr. 2010.

REISS, G. et al. **Advances in Polymer Synthesis**. New York: Springer US, 1985.

RIBEIRO, F. W. M. et al. Thermal and mechanical analyses of biocomposites from cardanol-based polybenzoxazine and bamboo fibers. **Journal of Thermal Analysis and Calorimetry**, v. 129, n. 1, p. 281–289, 21 jul. 2017.

RODRÍGUEZ, A. M. et al. Influence of Polarity and Activation Energy in Microwave-Assisted Organic Synthesis (MAOS). **ChemistryOpen**, v. 4, n. 3, p. 308–317, jun. 2015.

RUČIGAJ, A.; GRADIŠAR, Š.; KRAJNC, M. Kinetic investigation of a complex curing of the guaiacol bio-based benzoxazine system. **E-Polymers**, v. 16, n. 3, p. 199–206, 2016.

SAHOO, S.; MOHANTY, S.; NAYAK, S. K. Biobased polyurethane adhesive over petroleum based adhesive: Use of renewable resource. **Journal of Macromolecular Science, Part A**, v. 55, n. 1, p. 36–48, 2018.

SAINI, N. K.; AZECHI, M.; ENDO, T. Synthesis and Properties of Spiro-Centered Benzoxazines. **Macromolecules**, v. 48, n. 20, p. 7466–7472, 2015.

SARIKA, P. R. et al. Bio-Based Alternatives to Phenol and Formaldehyde for the Production of Resins. **Polymers**, v. 12, n. 10, p. 2237, 28 set. 2020.

SHABESTARI, M. E. et al. Effect of nitrogen and oxygen doped carbon nanotubes on flammability of epoxy nanocomposites. **Carbon**, v. 121, p. 193–200, 2017.

SHARMA, V. et al. Benzoxazine derivatives of phytophenols show anti-plasmodial activity via sodium homeostasis disruption. **Bioorganic & Medicinal Chemistry Letters**, mar. 2018.

SHELDON, R. A. Organic Synthesis - Past, Present and Future. **Chemistry & Industry (London)**, p. 903–906, 1992.

SHELDON, R. A. The E factor 25 years on: the rise of green chemistry and sustainability. **Green Chemistry**, v. 19, n. 1, p. 18–43, 2017.

SHELDON, R. A. Metrics of Green Chemistry and Sustainability: Past, Present, and Future. **ACS Sustainable Chemistry & Engineering**, v. 6, n. 1, p. 32–48, 2 jan. 2018a.

SHELDON, R. A. The Road to Biorenewables: Carbohydrates to Commodity Chemicals. **ACS Sustainable Chemistry & Engineering**, v. 6, n. 4, p. 4464–4480, 2 abr. 2018b.

SHEN, S. B.; ISHIDA, H. Synthesis and characterization of polyfunctional naphthoxazines and related polymers. **Journal of Applied Polymer Science**, v. 61, n. 9, p. 1595–1605, 29 ago. 1996.

SHIKOKU. **Benzoxazine**. Disponível em: http://www.shikoku.co.jp/eng/products/chemical/fine-chemical/benzoxazine.php. Acesso em: 25 set. 2018.

SHUKLA, S. et al. Cardanol benzoxazines – interplay of oxazine functionality (mono to tetra) and properties. **RSC Advances**, v. 5, n. 95, p. 78071–78080, 2015.

SINI, N. K.; BIJWE, J.; VARMA, I. K. Renewable benzoxazine monomer from Vanillin: Synthesis, characterization, and studies on curing behavior. **Journal of Polymer Science, Part A: Polymer Chemistry**, v. 52, n. 1, p. 7–11, 2014.

SOMISETTI, V. et al. Flexible, hard, and tough biobased polyurethane thermosets from renewable materials: glycerol and 10-undecenoic acid. **Journal of Coatings Technology and Research**, v. 15, n. 1, p. 199–210, 2018.

SPONTÓN, M. et al. Studies on thermal and flame retardant behaviour of mixtures of bis(m-aminophenyl)methylphosphine oxide based benzoxazine and glycidylether or benzoxazine of Bisphenol A. **Polymer Degradation and Stability**, v. 93, n. 12, p. 2158–2165, 2008.

TAKEICHI, T.; KAWAUCHI, T.; AGAG, T. High Performance Polybenzoxazines as a Novel Type of Phenolic Resin. **Polymer Journal**, v. 40, n. 12, p. 1121–1131, 15 dez. 2008.

TEONG, S. P.; YI, G.; ZHANG, Y. Hydroxymethylfurfural production from bioresources: past, present and future. **Green Chemistry**, v. 16, n. 4, p. 2015–2026, 2014.

THIRUKUMARAN, P. et al. Synthesis and characterization of new polybenzoxazines from renewable resources for bio-composite applications. **Polymer Composites**, v. 16, n. 2, p. 1–9, 2014.

TRAN, P.; NGUYEN, Q. T.; LAU, K. T. Fire performance of polymer-based composites for maritime infrastructure. **Composites Part B: Engineering**, v. 155, n. June, p. 31–48, dez. 2018.

TREJO-MACHIN, A. et al. Phloretic acid as an alternative to the phenolation of aliphatic hydroxyls for the elaboration of polybenzoxazine. **Green Chem.**, v. 19, n. 21, p. 5065–5073, 2017.

TRITA, A. S. et al. Synthesis of potential bisphenol A substitutes by isomerising metathesis of renewable raw materials. **Green Chem.**, v. 19, n. 13, p. 3051–3060, 2017.

TROST, B. M. The atom economy - a search for synthetic efficiency. **Science**, v. 254, n. 5037, p. 1471–1477, 1991.

VAFAEEZADEH, M.; HASHEMI, M. M. Polyethylene glycol (PEG) as a green solvent for carbon-carbon bond formation reactions. **Journal of Molecular Liquids**, v. 207, p. 73–79, 2015.

VAN GEMERT, D. et al. Cement concrete and concrete–polymer composites: Two merging worlds. **Cement and Concrete Composites**, v. 27, n. 9–10, p. 926–933, out. 2005.

VAN KREVELEN, D. . Some basic aspects of flame resistance of polymeric materials. **Polymer**, v. 16, n. 8, p. 615–620, ago. 1975.

VERMA, C. et al. Epoxy resins as anticorrosive polymeric materials: A review. **Reactive and Functional Polymers**, v. 156, p. 104741, nov. 2020.

VINITA, Y. **Yamamoto Vinita**. Disponível em: http://www.vinita.co.jp/en/advanced/technical_information/principle.html. Acesso em: 3 out. 2018.

VOIRIN, C. et al. Functionalization of cardanol: towards biobased polymers and additives. **Polym. Chem.**, v. 5, n. 9, p. 3142–3162, 2014.

WAHYUDIONO; SASAKI, M.; GOTO, M. Recovery of phenolic compounds through the decomposition of lignin in near and supercritical water. **Chemical Engineering and Processing: Process Intensification**, v. 47, n. 9–10, p. 1609–1619, set. 2008.

WANG, C.-F. et al. Low-Surface-Free-Energy Materials Based on Polybenzoxazines. **Angewandte Chemie International Edition**, v. 45, n. 14, p. 2248–2251, 27 mar. 2006a.

WANG, C.-F. et al. Stable Superhydrophobic Polybenzoxazine Surfaces over a Wide pH Range. **Langmuir**, v. 22, n. 20, p. 8289–8292, set. 2006b.

WANG, C. et al. Synthesis and copolymerization of fully bio-based benzoxazines from guaiacol, furfurylamine and stearylamine. **Green Chemistry**, v. 14, n. 10, p. 2799–2806, 2012.

WANG, Y.-X.; ISHIDA, H. Synthesis and Properties of New Thermoplastic Polymers from Substituted 3,4-Dihydro-2 H -1,3-benzoxazines. **Macromolecules**, v. 33, n. 8, p. 2839–2847, abr. 2000.

WANG, Z.; LIU, H.; LIU, S. Low-Dose Bisphenol A Exposure: A Seemingly Instigating Carcinogenic Effect on Breast Cancer. **Advanced Science**, v. 4, n. 2, p. 1600248, 2016.

WENDISCH, V. F.; KIM, Y.; LEE, J.-H. Chemicals from lignin: Recent depolymerization techniques and upgrading extended pathways. **Current Opinion in Green and Sustainable Chemistry**, v. 14, p. 33–39, 2018.

XU, H. et al. Hybrid polybenzoxazine with tunable properties. **RSC Advances**, v. 3, n. 11, p. 3677, 2013.

XU, Y. et al. Research status, industrial application demand and prospects of phenolic resin. **RSC Advances**, v. 9, n. 50, p. 28924–28935, 2019.

ZHANG, H. et al. Preparation of superhydrophobic polybenzoxazine/SiO2 films with self-cleaning and ice delay properties. **Progress in Organic Coatings**, v. 123, n. January, p. 254–260, out. 2018.

ZHANG, J. et al. Highly efficient, NiAu-catalyzed hydrogenolysis of lignin into phenolic chemicals. **Green Chem.**, v. 16, n. 5, p. 2432–2437, 2014.

ZHANG, L. et al. Cardanol-capped main-chain benzoxazine oligomers for resin transfer molding. **European Polymer Journal**, v. 93, n. June, p. 284–293, ago. 2017.

ZHU, L.; LI, N.; CHILDS, P. R. N. Light-weighting in aerospace component and system design. **Propulsion and Power Research**, v. 7, n. 2, p. 103–119, jun. 2018.

ZIRBES, M.; WALDVOGEL, S. R. Electro-conversion as sustainable method for the fine chemical production from the biopolymer lignin. **Current Opinion in Green and Sustainable Chemistry**, v. 14, p. 19–25, 2018.

3 DEVELOPMENT OF FULLY BIO-BASED HIGH-PERFORMANCE BIS-BENZOXAZINE UNDER ENVIRONMENTALLY FRIENDLY CONDITIONS

RESUMO

As preocupações ambientais estão impulsionando os cientistas na busca de produtos e processos mais sustentáveis. No desenvolvimento das bis-benzoxazinas, uma nova classe de resinas termofixas que está recebendo considerável atenção da academia e da indústria, o bisfenol-A (BPA) e os solventes tóxicos ainda são inconvenientes que precisam ser superados. Matérias-primas renováveis, solventes neotéricos e fontes de aquecimento com eficiência energética são soluções alternativas sofisticadas para as metodologias tradicionais. No presente estudo, é relatada uma abordagem ecologicamente correta de uma resina termofixo totalmente bio-baseada a partir de produtos derivados de lignocelulose. O catecol e a furfurilamina são fundidos com sucesso em bis-benzoxazinas em apenas alguns minutos sob irradiação de microondas na presença de poli (etilenoglicol) como solvente. O procedimento de processamento requer quantidades mínimas de metanol para purificação completa do produto com bons rendimentos, que é caracterizado por espectroscopia de infravermelho por transformada de Fourier (FTIR), calorimetria exploratória diferencial (DSC) e espectroscopia de ressonância magnética nuclear de ^{1}H e ^{13}C (RMN). Tal como utilizado no desenvolvimento de polímeros de alto desempenho, as novas polibenzoxazinas copolimerizadas são avaliadas por análise termogravimétrica (TGA) e análise mecânica dinâmica (DMA).

Palavras-chaves: Catecol. Polibenzoxazinas. Poli(etilenoglicol). Síntese assistida por micro-ondas. Química verde.

ABSTRACT

Environmental concerns are driving scientists in a quest for more sustainable products and processes. In the development of bis-benzoxazines, a novel class of thermosetting resins, which are receiving considerable attention from academia and industry, bisphenol A (BPA) and toxic solvents are still drawbacks that need to be overcome. Renewable feedstocks, neoteric solvents and energy-efficient heating sources are sophisticated alternative solutions to the current traditional methodologies. In the current study, an eco-friendly approach to a fully bio-based thermosetting resin from lignocellulose-derived products is reported. Catechol and furfurylamine are successfully fused into bis-benzoxazines in only a few minutes under microwave irradiation in the presence of poly(ethylene glycol) as a solvent. The workup procedure requires minimum amounts of methanol for complete purification of the product in good yields, which is characterized by Fourier transform infrared spectroscopy (FT-IR), differential scanning calorimetry (DSC) and ^{1}H and ^{13}C nuclear magnetic resonance spectroscopy (NMR). As used in the development of high-performance polymers, novel copolymerized polybenzoxazines are evaluated by thermogravimetric analysis (TGA) and dynamic mechanical analysis (DMA).

Keywords: Catechol. Polybenzoxazines. Poly(ethylene glycol). Microwave-assisted synthesis. Green chemistry.

Introduction

Thermosetting resins are key players in the advanced materials sector. Due to their high modulus, strength, durability and thermal and chemical resistances, thermosets provide high-performance products for industry. The most commonly used networks are phenolics, epoxy and polyester, especially in fields like civil infrastructure and transportation (RAQUEZ et al., 2010).

More recently, a novel class of commercially available thermosetting compounds, based on an aromatic oxazine ring, or benzoxazines, is being reported as a modern alternative for those classic resins (ISHIDA; AGAG, 2011).

When exposed to elevated temperature, benzoxazine monomers start to polymerize into polybenzoxazines, through a ring-opening polymerization (ROP) process, which does not require initiators or release by-products (FROIMOWICZ; ZHANG; ISHIDA, 2016; KISKAN; GHOSH; YAGCI, 2011; TAKEICHI; KAWAUCHI; AGAG, 2008).

Polybenzoxazines are now receiving a considerable attention from academia and industry, since they present outstanding characteristics, such as near-zero shrinkage upon polymerization, high glass-transition temperature (Tg), excellent thermal and mechanical properties, flame retardancy, and low surface energy (FROIMOWICZ et al., 2016; HASSAN et al., 2016; LIN et al., 2017; WANG et al., 2006b).

Another interesting aspect of benzoxazine resins is their great versatile synthetic routes. Since it uses a phenolic compound, a primary amine and formaldehyde as starting materials, a wide range of reactants can be employed. Depending on the starting materials, the property of such resins, and hence of their polymers, can be tailored for the required applications (DUMAS et al., 2016b; LI et al., 2012; SAINI; AZECHI; ENDO, 2015; WANG et al., 2006a; ZHANG et al., 2017).

Bisphenol A (BPA)-based benzoxazine is considered a standard due to easy availability in high purity and inexpensive nature of BPA. BPA is one of the highest-volume monomers currently produced, on about 4.5 million tons per annum scale, but has been raising many health concerns due to its endocrine activities in humans (TRITA et al., 2017). An increasing number of recent studies have shown that even BPA alternatives, like bisphenol S (BPS) and bisphenol F (BPF), present comparable effects on the endocrine system as BPA itself (GRAMEC SKLEDAR; PETERLIN MAŠIČ, 2016).

For bis-benzoxazines synthesis, an organic solvent is generally required to overcome technical restrictions, e.g. high viscosity, high melting points, or poor solubility of reactants. Furthermore, the commonly used solvents are toxic, such as toluene, p-xylene or dioxane, are toxic. It is also usual for the reaction time of these procedures to last for hours or even days under traditional heating (CHIU et al., 2016; SAINI; AZECHI; ENDO, 2015).

Not only health but also environmental concerns are driving scientists and researchers in a quest to replace traditional petroleum-derived chemicals and materials. In the contemporary society, novel processes and products must be designed aiming not only for their immediate applications but also incorporating their footprints for future generations. With the advent of "green chemistry", Anastas and Warner provided a guidance to help chemists in achieving this goal (ANASTAS; WARNER, 1998). Based on these principles, sophisticated approaches to overcome these barriers could include the use of (i) renewable feedstock (e.g. biomass residues); (ii) neoteric solvents (e.g. ionic liquids (IL) or polyethylene glycol (PEG)); and (iii) more energy-efficient heating sources, like microwave irradiation.

Many attempts have been made towards the sustainable development of benzoxazines. The utilization of bio-based renewable feedstock has allowed the emergence of many novel and promising benzoxazine monomers through the exploration of both biomass-derived building blocks: phenols and amines (LLIGADAS et al., 2014).

Furfurylamine (fu), or 2-(aminomethyl)furan, is an example of a bio-based amine that makes possible the synthesis of eco-friendly benzoxazines, generating polymers with excellent properties (AMBROŽIČ; ŠEBENIK; KRAJNC, 2015). Furfurylamine can be easily obtained from furfural, which is a well-known platform chemical produced on industrial scales from the decomposition of carbohydrate materials and listed as the top 10 value-added bio-based chemicals by the US Department of Energy (TEONG; YI; ZHANG, 2014).

Several naturally occurring phenolic compounds have also been reported as alternatives to BPA. Cardanol,(A. ATTANASI et al., 2012; CALÒ et al., 2007; KOTZEBUE et al., 2016) urushiol,(XU et al., 2013) vanillin,(SINI; BIJWE; VARMA, 2014) guaiacol (PHALAK; PATIL; MHASKE, 2017), eugenol (DUMAS et al., 2015) and coumarins (FROIMOWICZ et al., 2016) were thoroughly studied as starting materials for the synthesis of benzoxazine monomers and converted into polybenzoxazines.

Nevertheless, to the best of our knowledge, there are still no reports in the scientific literature on the synthesis of bis-benzoxazines starting with catechol (CT). Chemically described as 1,2-dihydroxybenzene, CT is a renewable raw material that can be obtained from lignin by different chemical processes (BILAL et al., 2017; CHEN; WAN, 2017; JEENPADIPHAT; MONGKOLPICHAYARAK; TUNGASMITA, 2016). Recent results published by Dumas and co-workers, addressing the synthesis of bis-benzoxazines based on resorcinol and hydroquinone

(DUMAS et al., 2016b), indicate catechol as a promising alternative renewable starting material for the synthesis of high-performance polymers.

In the case of neoteric solvents, poly(ethylene glycol) (PEG) was already employed as a reactant in previous syntheses of benzoxazines (BROWN; RIDER, 2017; TREJO-MACHIN et al., 2017), but not as an inert and innocuous reaction media. Being a non-toxic polyether compound, which is available commercially in a variety of molecular weights and has been approved by U.S. Food and Drug Administration (FDA) for internal consumption,(HARRIS, 1992) PEG has unique properties that turn it in an idiosyncratic alternative to traditional organic solvents. They are biodegradable, non-volatile, low flammability, highly stable to acid, base and high temperatures; may be recovered by extraction or by direct distillation; and are soluble in polar and non-polar solvents, but insoluble in aliphatic hydrocarbons (CHEN et al., 2005; VAFAEEZADEH; HASHEMI, 2015). Another important peculiarity is its high capacity to absorb microwave (MW) radiation (CINI; PETRICCI; TADDEI, 2017; DRIOWYA et al., 2016). In microwave-assisted organic synthesis (MAOS), which uses microwave irradiation as a heating source due to the effective heating of certain materials (reactants or solvent) by the "microwave dielectric heating effects", it is possible to drastically reduce reaction time, decrease by-product formation and, consequently, increase product purity (KAPPE, 2004).

Based on the above, we report the microwave-assisted synthesis of a fully bio-based bis-benzoxazine, starting from two lignocellulose-based bio-products, catechol and furfurylamine, having PEG as a solvent. In order to extend this methodological procedure for more frequently employed phenols, the well-known BPA was also evaluated as a control under these new conditions. The obtained monomers were structurally characterized by Fourier transform infrared spectroscopy (FTIR), and ^{1}H and ^{13}C nuclear magnetic resonance spectroscopy (NMR). In view of the great potential of bis-benzoxazines in the development of high-performance materials, the thermal behaviours of these monomers were also investigated by differential scanning calorimetry (DSC). After spectral and thermal characterization, their copolymers were analyzed by thermogravimetric analysis (TGA) and dynamic mechanical analysis (DMA).

Experimental Section

Materials and methods

Catechol (99%), bisphenol-A (97%), furfurylamine (99%) and paraformaldehyde (95%) were used as received by Sigma-Aldrich without any purification. Poly(ethylene glycol) (PEG) (Kollisolv® PEG E 400) of M_n = 400 Da was used as received by Aldrich.

Analytical methods

^{13}C and ^{1}H nuclear magnetic resonance spectroscopy (^{1}H NMR and ^{13}C NMR)

The ^{1}H NMR and ^{13}C NMR spectra were recorded on BRUKER spectrometer, model Avance DPX, operating at 300 MHz for ^{1}H and at 75 MHz for ^{13}C. Deuterated chloroform ($CDCl_3$) was used as the solvent to solubilize the samples, and tetramethylsilane (TMS) was used as an internal standard.

Fourier Transform Infrared Spectroscopy (FTIR)

The FTIR spectra were obtained on a PerkinElmer spectrometer model FTIR/NIR FRONTIER, using an attenuated total reflectance (ATR) accessory with zinc selenide (ZnSe) crystal surface, and resolution of 4 cm^{-1} using the arithmetic average of four scans in the wavenumber range of 4000–650 cm^{-1}.

Differential Scanning Calorimetry (DSC)

The DSC analyses were performed on a Mettler-Toledo DSC 823e, under a N_2 atmosphere (flow rate of 50 mL/min). For the characterization of the monomers, the non-isothermal measurements were performed with a heating rate of 10 °C/min, in a temperature range of 30 - 400°C, using approximately 5 mg of samples. All the analyses were performed using aluminum crucibles.

Thermogravimetric analysis (TGA)

TGA analyses were performed on a Mettler-Toledo TGA/SDTA 851e, conducted under N_2 atmosphere (flow rate of 50 mL/min) with a heating rate of 10 ºC/min in a temperature range of 30 to 800ºC. Alumina crucibles were used with approximately 5 mg of samples.

Dynamic mechanical analysis (DMA)

DMA were conducted on Mettler-Toledo DMA-1, using a single cantilever mode, at a heating rate of 5 ºC min^{-1} from 30 to 300ºC, using a frequency of 1 Hz in air. The deformation was within the linear viscoelastic limit, determined by a strain sweep test.

Microwave-assisted organic syntheses (MAOS)

The microwave-assisted organic syntheses (MAOS) were performed in a Milestone microwave reactor, model StartSYNTH, operating in an open-vessel configuration at a frequency of 2.45 GHz. The temperature set was controlled by a contact-less infrared sensor, and the power applied was limited to 850 W.

3,8-bis(furan-2-ylmethyl)-2,3,4,7,8,9-hexahydrobenzo[1,2-e:4,3-e']bis([1,3]oxazine) (CT-fu)

To a 50 mL round bottom flask equipped with a stirring bar was added PEG-400 (25 mL), catechol (5.00 g, 45.86 mmol), furfurylamine (8.58 mL, 91.75 mmol) and paraformaldehyde (7.24 g, 229,37 mmol). The flask was placed in a microwave cavity and fitted with a Vigreux column. The microwave was set to a maximum power of 850 W, the temperature was programmed to increase from room temperature to 120 ˚C in a period of 2 minutes; and kept at this temperature for additional 5 minutes, totaling 7 minutes under microwave irradiation. After the completion of the reaction, the mixture was cooled to room temperature forming a bulky solid phase. This mixture was washed with methanol (4 X 75 mL) and then filtered. After solvent evaporation, 9.22 g (60 % yield) of a white powder was obtained and characterized as **CT-fu**.

^{1}H NMR (300 MHz, $CDCl_3$, δ ppm): 7.42 (d, *J* = 2 Hz, 1H, Ar H), 6.51 (s, 1H, Ar H), 6.34 (m, 1H, Ar H), 6.27 (m, 1H, Ar H), 4.99 (s, 2H, O-CH_2-N), 4.00 (s, 2H, N-CH_2-Fu), 3.97 (s, 2H, N-CH_2-Ar); **^{13}C NMR** (75 MHz, $CDCl_3$, δ ppm): 151.8, 142.7, 119.0, 118.7, 110.4, 109.1, 82.7 (O-

CH_2-N), 49.3 (Ar-CH_2-N), 48.6; **FT-IR** (ATR-ZnSe, cm^{-1}): 1577 (stretching of furan ring), 1478 (stretching of tetrasubstituted benzene ring), 1235 (C-O-C asymmetric stretching), 923 (benzoxazine related mode). **Elemental Analysis:** C (68.17 %), H (5.72 %), N (7.95 %) (calculated); C (67.53 %), H (5.99 %), N (7.80 %) (found). **Molecular weight:** 352.38 $g.mol^{-1}$

6,6'-(propane-2,2-diyl)bis(3-(furan-2-ylmethyl)-3,4-dihydro-2H-benzo[e][1,3]oxazine) **(BA-fu)**

The method used to synthesize **BA-fu** was an improved method of Liu and co-workers (2015) which used conventional heating. To a 25 mL round bottom flask equipped with a stirring bar was added PEG-400 (10 mL), bisphenol A (2.00 g, 8.50 mmol), furfurylamine (1.53 mL, 17.00 mmol) and paraformaldehyde (1.34 g, 42.50 mmol). The flask was placed in a microwave cavity and fitted with a Vigreux column. The microwave was set to a maximum power of 850 W, the temperature was programmed to increase from room temperature to 120°C in a period of 2 minutes; and kept at this temperature for additional 5 minutes, totaling 7 minutes under microwave irradiation. After the completion of the reaction, the mixture was cooled to room temperature and then diluted in 100 mL of ethyl acetate. The organic phase was treated with an aqueous solution of sodium hydroxide 2 mol L^{-1} (3 X 50 mL) and then with distilled water (3 X 50 mL). The organic phase was dried over sodium sulphate, filtered and concentrated under reduced pressure to give a yellowish viscous resin. This material was recrystallized with 85 mL of a solvent mixture (hexane:ethyl acetate, 20:1), affording 2.03 g (51% yield) of white crystals characterized as **BA-fu**.

^{1}H NMR (300 MHz, $CDCl_3$, δ ppm): 7.42 (m, 1H; Ar H), 6.99 (dd, *J* = 9 Hz, *J* = 3 Hz, 1H, Ar H), 6.83 (d, *J* = 3 Hz, 1H, Ar H), 6.73 (d, *J* = 9 Hz), 6.35 (m, 1H, Ar H), 6.26 (m, 1H, Ar H), 4.86 (s, 2H, O-CH_2-N), 4.00 (s, 2H, N-CH_2-Fu), 3.95 (s, 2H, N-CH_2-Ar), 1.62 (s, 3H, CH_3); **^{13}C NMR** (75 MHz, $CDCl_3$, δ ppm): 151.9, 143.4, 142.7, 126.5, 125.7, 119.0, 116.1, 110.4, 109.0, 81.9 (O-CH_2-N), 50.2 (Ar-CH_2-N), 48.5, 42.0, 31.3; **FTIR** (ATR-ZnSe, cm^{-1}), cm^{-1}: 1577 (stretching of furan ring), 1495 (stretching of trisubstituted benzene ring), 1230 (C-O-C asymmetric stretching), 928 (benzoxazine related mode). **Elemental Analysis:** C (74.02 %), H (6.43 %), (5.95 %) (calculated); C (73.66 %), H (6.29 %), N (5.87 %) (found). **Molecular weight:** 470.56 $g.mol^{-1}$

Preparation and (co)polymerization of the bis-benzoxazines

Three resins were produced containing different amounts of **CT-fu** and **BA-fu**: **CT/BA10** (10% **CT-fu** and 90% **BA-fu**), **CT/BA30** (30% **CT-fu** and 70% **BA-fu**), **CT/BA50** (50% **CT-fu** and 50% **BA-fu**). For the (co)polymerization of the bio-based resins, each sample was added to silicone molds (40 X 20 X 2 mm) and then melted and polymerized. The obtained polymers were produced using the following heating schedule: 120 ºC (1 h), 140 ºC (1 h), 160 ºC (1 h), 180 ºC (1 h) and 200 ºC (2h). The obtained polybenzoxazines were removed from the mold and then put to post curing at 220 ºC (2 h) and 240 ºC (2 h).

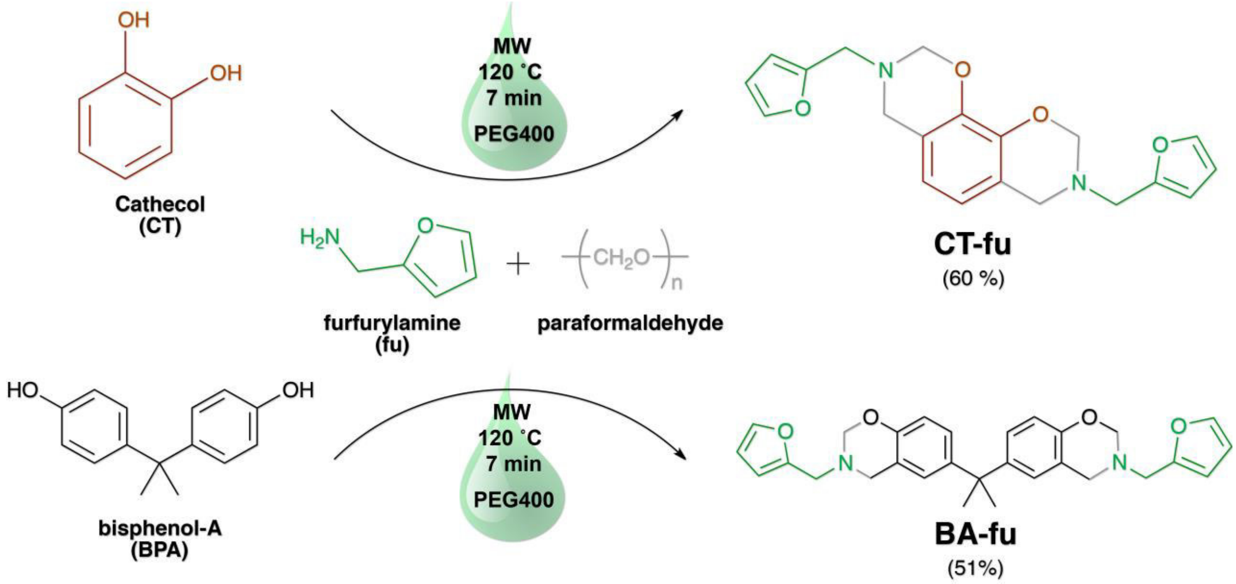
Results and Discussion

Design of sustainable development of bio-based bis-benzoxazines

The bis-benzoxazines were obtained by using a one-pot synthesis of catechol (or BPA), furfurylamine and paraformaldehyde as shown in Scheme 3. As is frequently observed and reported for the synthesis of bis-benzoxazines, these reactants produced a viscous reaction media, making it very difficult to be homogenized by stirring, and therefore, as an eco-friendly solution for the traditional solvents, a small amount of PEG400 was used.

In many cases, bis-benzoxazine syntheses are performed in the presence of organic solvents in order to keep the reaction media homogeneous since, depending on the compounds involved, high viscosity and/or low miscibility could prevent the maintenance of local stoichiometry and successful occurrence of the reaction. Therefore, utilization of a solvent is needed (LIN et al., 2017).

Scheme 3 - Synthetic scheme for bis-benzoxazines **CT-fu** and **BA-fu**.



Source: The Author

In this work, PEG was not only successfully employed as an alternative non-toxic solvent, but its unique properties allowed us to (*i*) promptly synthesize a fully bio-based bis-benzoxazine in only seven minutes under microwave irradiation; and (*ii*) to easily isolate the product by simply filtering and washing with small portions of methanol, which was completely recycled through rotatory evaporation by the end of purification procedure.

The intermolecular forces that predominate between PEG molecules are of hydrogen bonds and dipole-dipole types. These kinds of forces promote better interactions among polar, or relatively polar, substances – as catechol (**CT**), furfurylamine (**fu**) and formaldehyde – but are unable to effectively interact with non-polar compounds, which is the case of the desired product (**CT-fu**), in which intermolecular interactions are basically driven by π-stacking, promoting the formation of more compact and rigid structure (MARTINEZ; IVERSON, 2012). Due to these properties, solvent cooling and the simple addition of small amounts of methanol were sufficient for the complete precipitation of the product.

Due also to its high capacity to convert MW radiation into heat, PEG proved to be an outstanding reaction media for microwave-assisted organic synthesis, reducing drastically the reaction time and the amount of energy required to promoting its efficient heating. The likelihood of the ring closure of an open Mannich base into oxazine ring depends on the dielectric constant of the solvent, being smaller the dielectric constant the higher the probability of ring closure. The dielectric constant of PEG is approximately 8-12, and thus it does not interfere significantly the ring closure reaction (AGAG; JIN; ISHIDA, 2009).

Bis-benzoxazines can be synthesized under microwave irradiation (MANIKANNAN; MUTHUSUBRAMANIAN, 2010) and, more recently, our group reported a systematic study on the microwave-assisted synthesis of mono-functional benzoxazines under solvent-free conditions (OLIVEIRA et al., 2017) from which the actual parameters reported here were based.

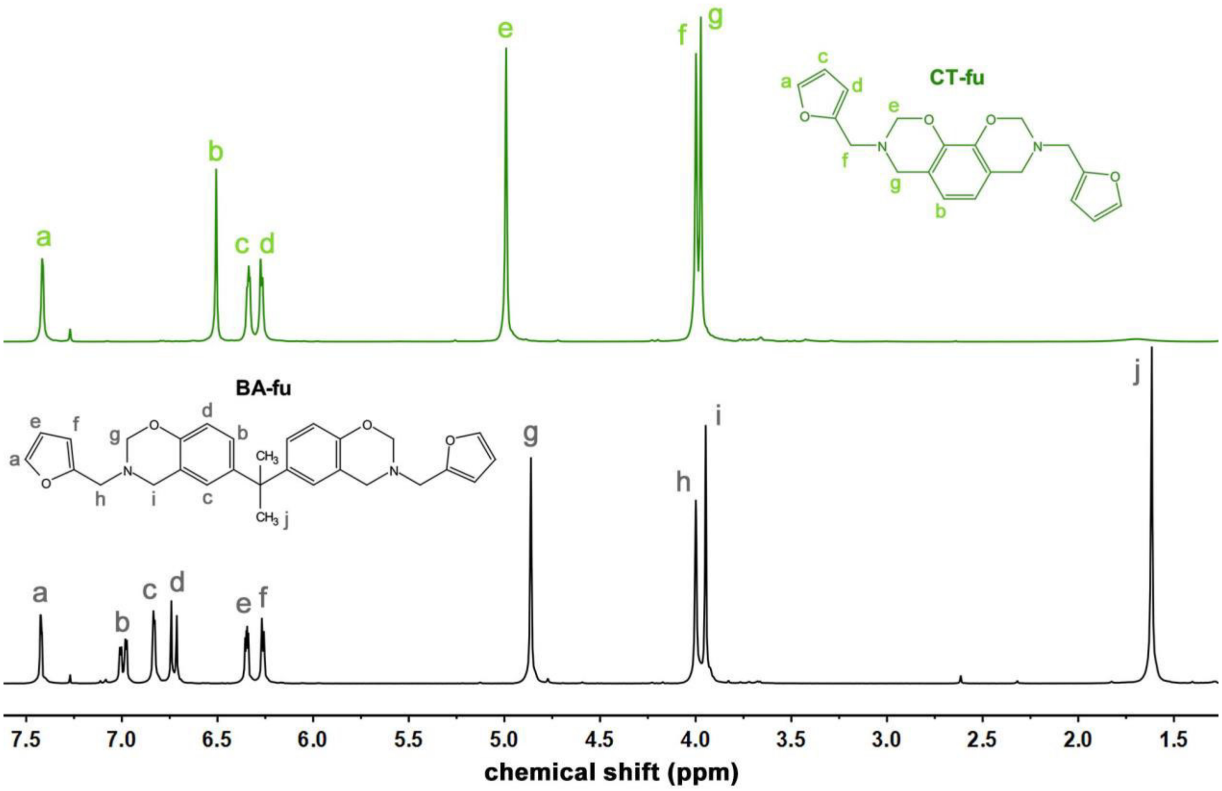
To validate and expand the applicability of the procedure described, we also reproduced these conditions using BPA as the phenolic moiety instead of catechol (Scheme 1). The method proved to be very effective also for the synthesis of the partially bio-based bis-benzoxazine **BA-fu**. It further points to a possibility that the approach described in the current paper might be universally applicable to many other benzoxazines. When compared to a previously reported synthetic methodology (LIU; CHOU, 2005), which used dioxane as a solvent and traditional heating for 24 hours, the procedure described here provided the same product in similar yields, but with dramatic reduction of time and under eco-friendly conditions.

Under these circumstances, both the product and process described in this work proved to be very effective and highly eco-friendly, as featured by: (a) the use PEG as an innocuous and inexpensive solvent; (b) of microwave irradiation as a heating source; (c) much shorter reaction times; (d) no use of catalyst or auxiliary reactants; and (e) good yields. These aspects are properly inserted within the Green Chemistry principles, which emphasize, among others, the use of renewable feedstock, safer solvents, energy efficiency and atom economy (ANASTAS; WARNER, 1998).

Structural characterization of bis-benzoxazines

The molecular structures of the monomers were confirmed by ^{1}H (Figure 20) and ^{13}C NMR (Figure 21) and by FTIR. It was noticed that the chemical shifts of the oxazinic methylenes were very similar by analyzing the ^{1}H and the ^{13}C NMR spectra. In the ^{1}H NMR spectra, the structures of the obtained products were confirmed by the presence of the two singlets in the regions of 5.10 to 4.80 ppm and 3.98 to 3.93 ppm, which represents the two methylenes of the oxazinic group. The chemical structure of **CT-fu** was compared with the **H-fu** and **R-fu** of Dumas and coworkers(DUMAS et al., 2016b) and it was shown that **CT-fu** did not have any isomer or oligomers such as of **H-fu** and **R-fu**.

Figure 20 - ^{1}H NMR spectra of **CT-fu** and **BA-fu**



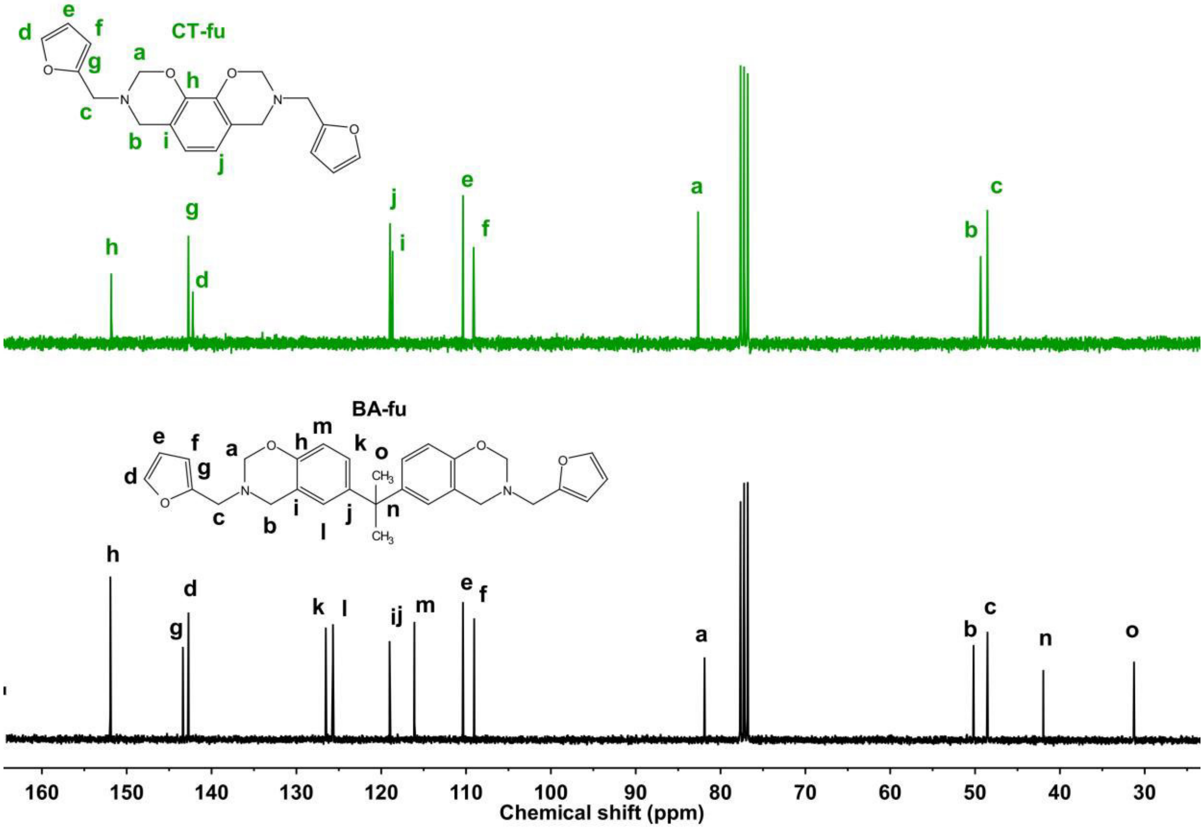
Source: The author

The presence of the oxazinic methylenes was also confirmed by ^{13}C NMR spectra with the peaks at around 82 and 50 ppm.

One of the concerns about this synthetic procedure was that side-products could be formed after a possible nucleophilic attack from the terminal hydroxyl groups of PEG to the oxazine ring. But, recently, Brown and Rider (BROWN; RIDER, 2017) described the utilization of poly(ethylene glycol) as a grafting agent for the synthesis of low T_g polybenzoxazines and no interaction from PEG's hydroxyl end-group to the oxazine was observed.

As the NMR spectra demonstrate, PEG was not incorporated in the monomer, indicating its low reactivity in the reported conditions and, therefore, can be efficiently used as a solvent.

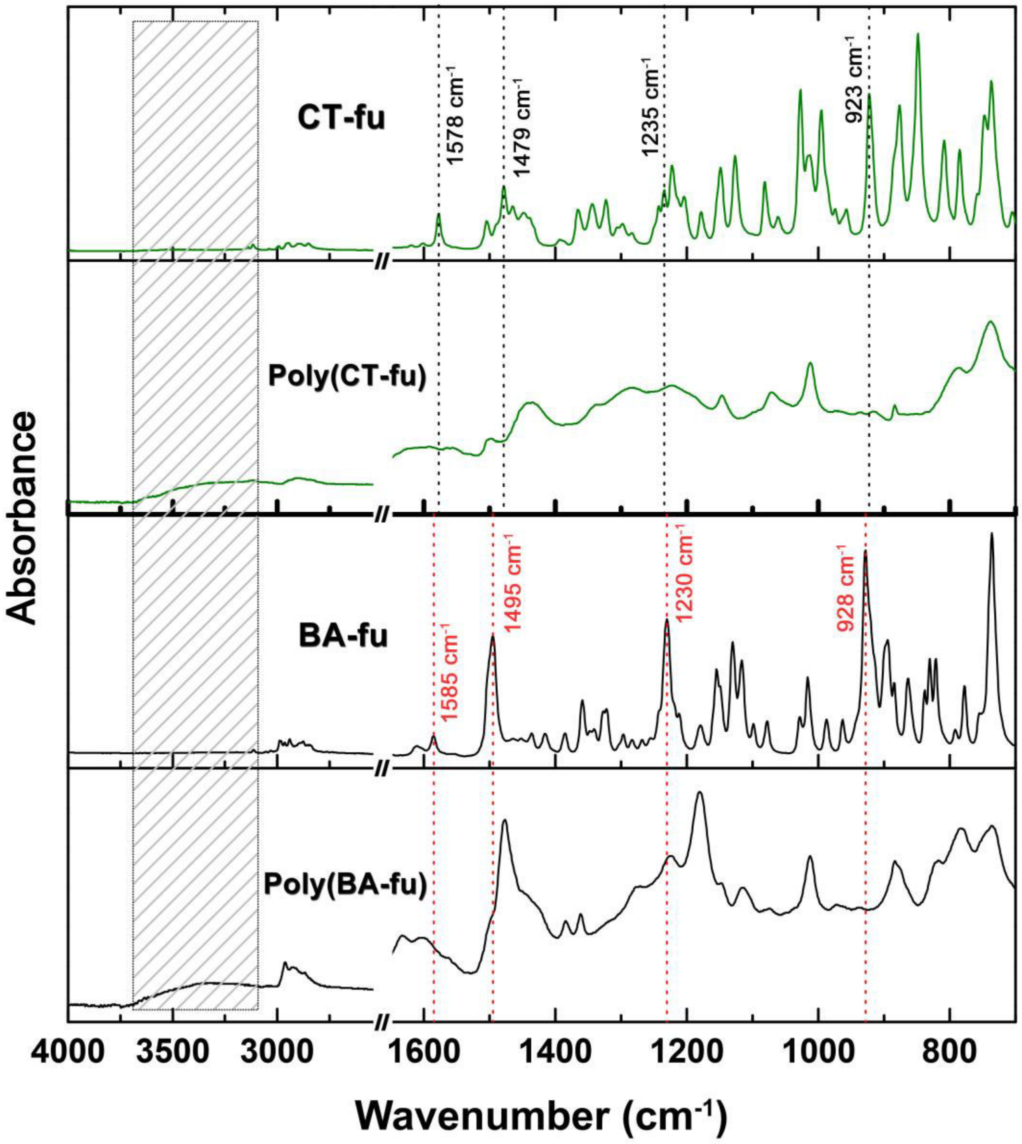
Figure 21 - ^{13}C-NMR spectra of **CT-fu** and **BA-fu**.



Source: The Author

In Figure 22 are shown the FTIR spectra of **CT-fu** and **BA-fu** and their respective polymers, **poly(CT-fu)** and **poly(BA-fu)**, which were necessary for a better understanding of the vibrational modes of the bis-benzoxazines and their polybenzoxazines.

Figure 22 - FTIR spectra of **CT-fu** and **BA-fu**.



Source: The Author

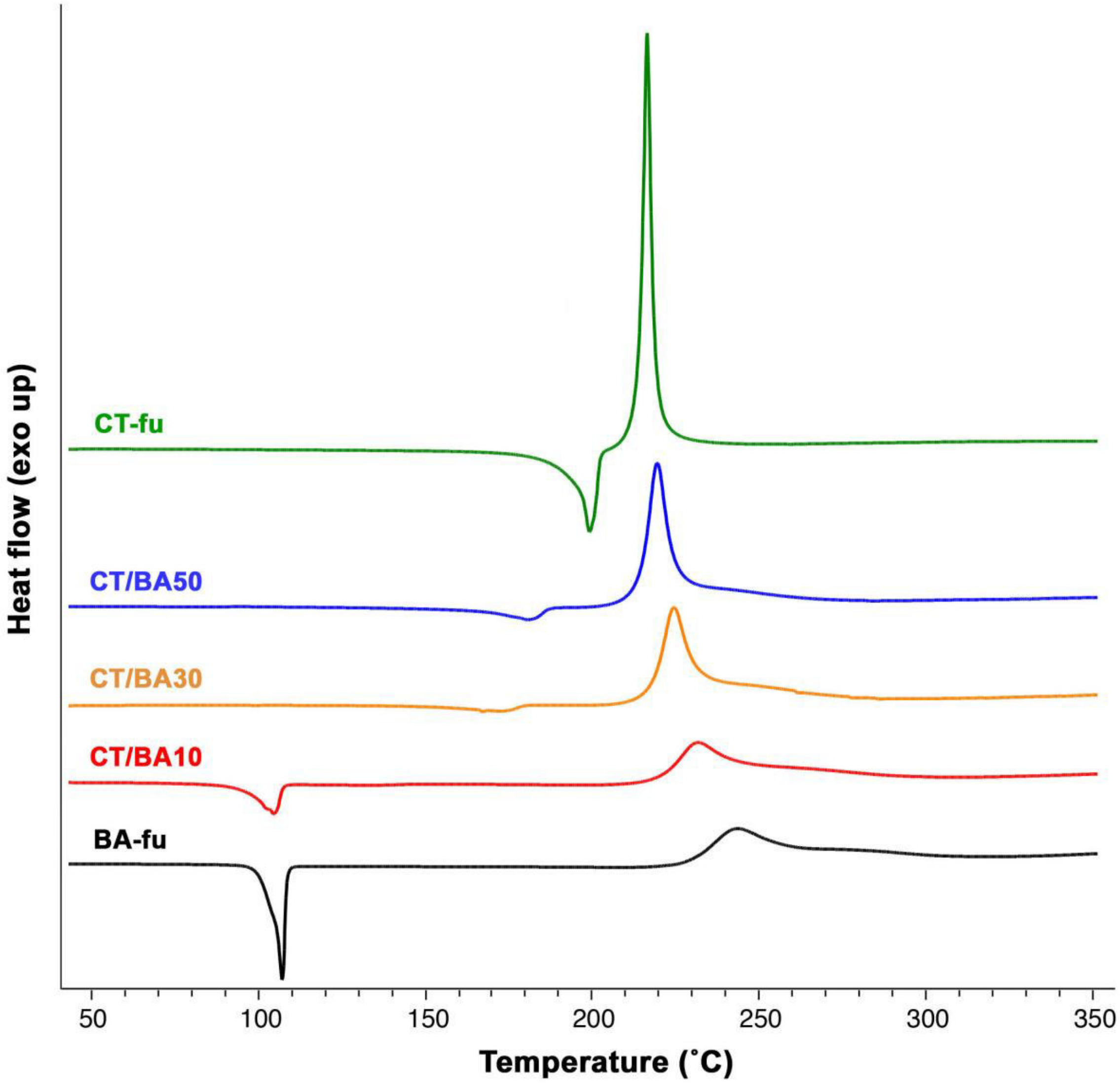
The absence of the bands from the region between 3100 to 3600 cm^{-1} confirms that the hydroxyl groups are not present on the monomers, suggesting the transformation into bis-oxazine rather than mono-oxazine structure. The band at 1479 cm^{-1} is attributed to the tetrasubstituted benzene ring of **CT-fu**, and the band at 1495 cm^{-1} is attributed to the trisubstituted benzene ring of **BA-fu**. The presence of the oxazine ring was observed by the C-O-C asymmetric stretching modes of the bands at 1235 cm^{-1} for **CT-fu** and 1230 cm^{-1} for **BA-fu,** and also by the benzoxazine related mode(HAN et al., 2017) at 923 and 928 cm^{-1} for **CT-fu** and **BA-fu**, respectively. The presence of the furan ring in the structure of **CT-fu** and **BA-fu** was confirmed by the appearance of bands at 1578 cm^{-1} and 1585 cm^{-1}, respectively (LIU; CHOU, 2005). Also in the FTIR spectra, the absence of a broad and intense band at 1094 cm^{-1} indicates no insertion of PEG in the molecular structures of the products.

After polymerization of the monomers, it was observed the disappearance of the bands regarding the C-O-C asymmetric stretching (around 1230 cm^{-1}) and the benzoxazine related modes (around 920 cm^{-1}), confirming the successful cleavage of the oxazine ring. After the ring-opening process of **CT-fu**, it was also observed that the electrophilic substitution occurred on the substituted benzene rings of the benzoxazines, as their respective bands disappeared, while for **BA-fu** the respective bands were displaced to lower wavenumbers. Another observation made was the broad absorption around 1610 cm^{-1}, which indicate that electrophilic substitutions occurred also on the furfuryl groups (LIU; CHOU, 2005).

Polymerization behavior of the bis-benzoxazines

The thermal behavior of the bis-benzoxazines monomers was monitored by DSC (Figure 23). The obtained data are summarized in Table 2.

Figure 23 - DSC curves of CT-fu, BA-fu and different resins compositions (CT-fu/BA-fu).



Source: The author

Table 2 - Data of DSC curves of **CT-fu**, **BA-fu** and different resins compositions (**CT-fu/BA-fu**).

Sample	T_m (°C)	T_o (°C)	T_p (°C)	ΔH_p (J g^{-1})	ΔH_p (kJ mol^{-1})
CT-fu	198	213	220	381	134.1
BA-fu	105	223	240	246	115.6
CT/BA10	104	220	232	251	-
CT/BA30	167	216	225	331	-
CT/BA50	181	214	221	346	-

Source: The author

It was observed that the endothermic events, which represent the melting points (T_m), of the two bis-benzoxazines were quite distinct. The m.p. of **CT-fu** was higher than that of **BA-fu**, which was expected since both oxazine rings of **CT-fu** are fused to the same benzene, making it a much more rigid and compact molecule when compared to **BA-fu**, where the oxazine rings are separated by an alkyl bridge, which gives flexibility to this structure.

The exothermic events, corresponding to the temperature range of the ring-opening polymerization (ROP) of the monomers, demonstrated also different behaviors. While the **BA-fu** monomer exhibits a broad exothermic event between 220 and 300°C, with an initial polymerization temperature (T_o) at 223°C, the **CT-fu** monomer has a sharp exothermic event between 205 and 240°C, with T_o at 213°C. It was also observed that the enthalpy of polymerization value (ΔH) of **CT-fu** is more than 50 % greater than that obtained for **BA-fu**. The obtained results for **BA-fu** are consistent with those reported by Liu and Chou (LIU; CHOU, 2005).

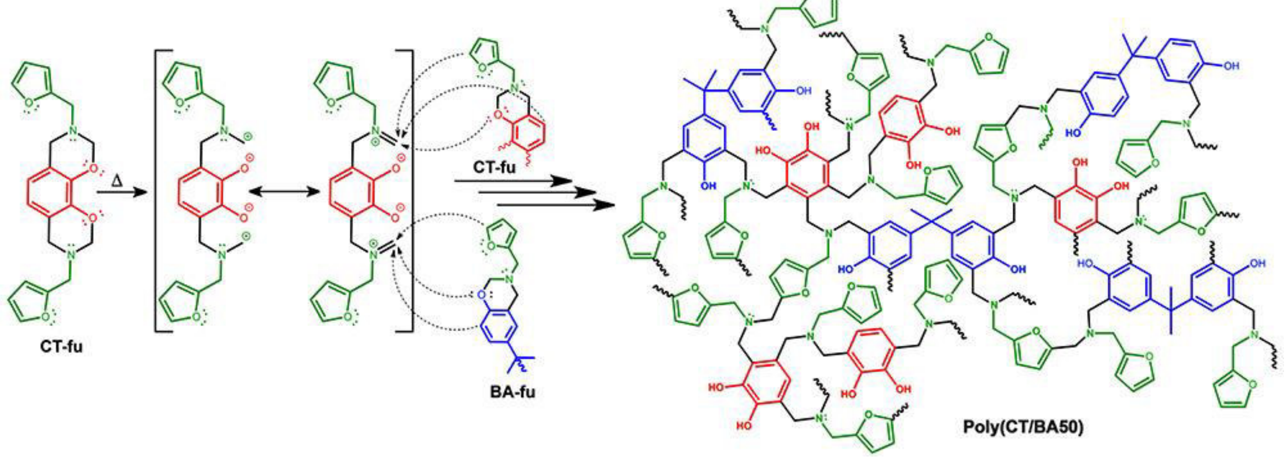
Due to the proximity of the fusion and polymerization events (processing window) of **CT-fu**, it becomes very difficult to process the monomer in order to obtain an intact and defects-free polymer. A strategy to solve this problem is by polymerizing the monomer under high pressure(SHEN; ISHIDA, 1996) or by copolymerizing this monomer with another one that possesses a lower melting point. Thus, it was proposed to blend the two bis-benzoxazines in different concentrations, which could lead to resins with better processing windows, and therefore to high-quality polybenzoxazines samples, liable to have their mechanical properties analyzed by DMA.

For this, three different resin compositions were prepared, as described in the Experimental Section, namely: **CT/BA10**, **CT/BA30** and **CT/BA50.**

Analyzing the DSC thermograms of the monomer mixtures (Figure 23), it was noticed only one endothermic event, indicating that the monomers are well compatible to be fused simultaneously.

It was also observed that with the increased content of **CT-fu**, the polymerization peak temperature (T_p) was decreased, while the extrapolated onset polymerization temperature (T_o) was practically maintained. This demonstrates that the polymerization initiates with the oxazine ring-opening of **CT-fu**, catalyzing the polymerization process of **BA-fu,** as depicted in Scheme 4. These polymerization behaviors of the resins were expected since **CT-fu** has a lower polymerization temperature than **BA-fu**.

Scheme 4 - Representative copolymerization mechanism of CT-fu and BA-fu



Source: The author

Thermal analysis of the bio-based polybenzoxazines

The thermal stability of polybenzoxazines was evaluated by thermogravimetric analysis (TGA) under an inert atmosphere (N_2). The TGA thermograms of **poly(BA-fu)**, **poly(CT/BA10)**, **poly(CT/BA30)** and **poly(CT/BA50)** are shown in Figure 24 and their data summarized in Table 3. Analyzing the extrapolated onset degradation temperature (T_D) it was noticed that **poly(BA-fu)** present a higher initial degradation than its copolymers with **CT-fu**. Nevertheless, as the **CT-fu** content increased, the char yields (*CY*) values of the copolymers were also increased. The copolymer with the highest bio-based content, **poly(CT/BA50)**, had a 14 % increase in char yield when compared with **poly(BA-fu)**.

Compared to results previously published for the classical bisphenol A/aniline **(BA-a or P-BPA-ABz)** based polybenzoxazine,(DAYO et al., 2017; DOUSE et al., 2016; HASSAN et al., 2016; KOPSIDAS; HAMERTON, 2016) the polybenzoxazines reported in this work presented superior thermal stability. With the incremental incorporation of **CT-fu** into **BA-fu**, not only the biomass-derived content was increased (up to 50% w/w), but, especially, the generation of carbonaceous residue (*CY*).

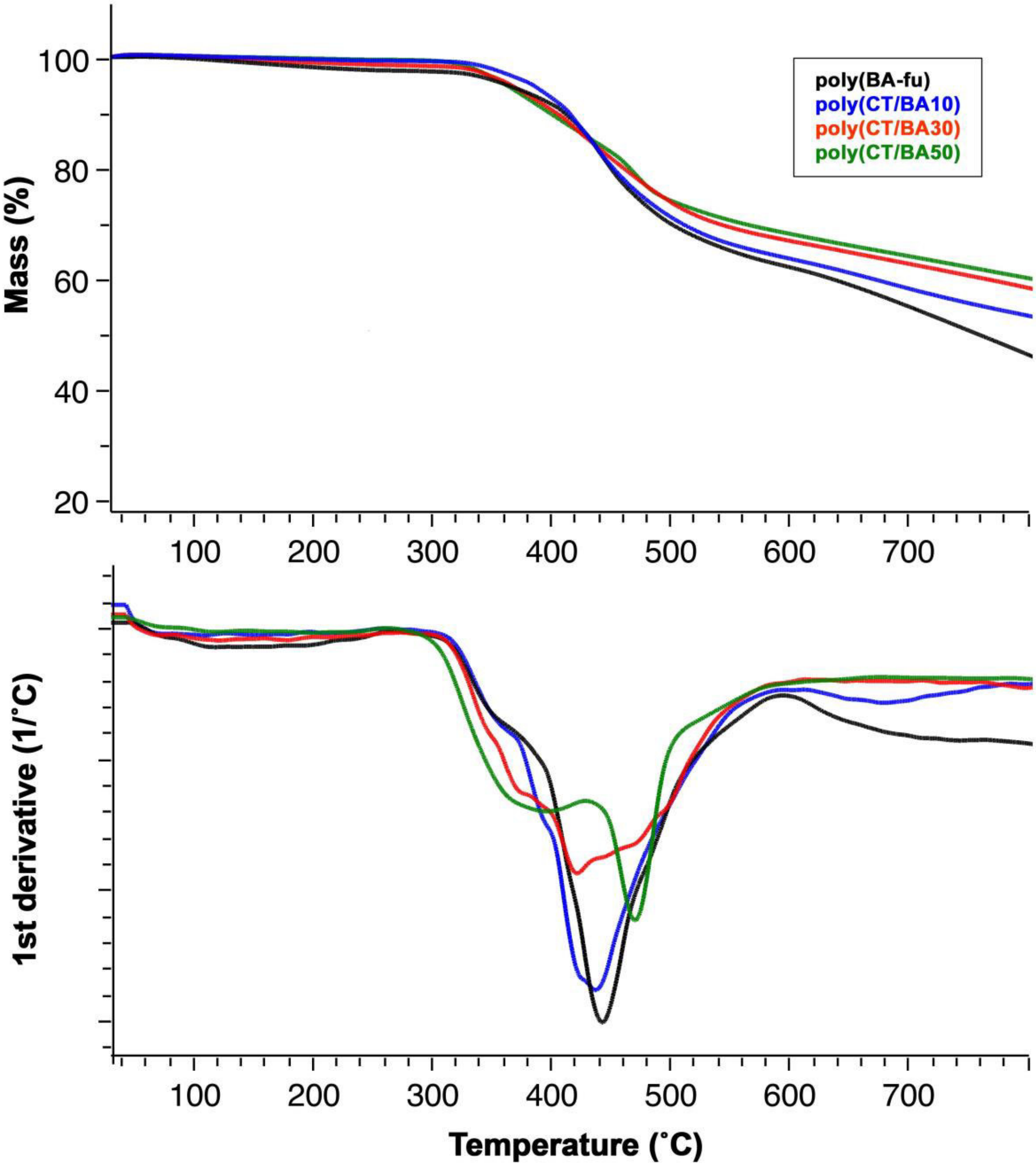
Table 3 - Data of TGA curves of poly(BA-fu), poly(10%) and poly(30%), poly(50%).

Name	**T_D (ºC)**	**T_5 (ºC)**	**T_{10} (ºC)**	**T_{20} (ºC)**	***CY* (%)**	***LOI****
poly(BA-fu)	338	361	410	444	46	35.9
poly(CT/BA10)	336	384	414	443	53	38.7
poly(CT/BA30)	331	365	403	446	58	40.7
poly(CT/BA50)	329	361	397	458	60	41.5

*Calculated from the char yield at 800 ºC of TGA analysis.

Source: The author

Figure 24 - TGA curves of poly(BA-fu), poly(CT/BA10), poly(CT/BA30) and poly(CT/BA50).



Source: The author

Considering the elevated values of char yield observed, TGA results were also employed to evaluate the flame retardancy of the polybenzoxazines by the determination of the limiting oxidation index (*LOI*), which is the minimum O_2 concentration to let the material ignite to cause flammability. Materials with *LOI* values ≤ 26 are considered flammable and an interesting way to estimate LOI values of halogen-free polymers is by using the char yields of TGA analyses using the van Krevelen equation (Eq. 2) (VAN KREVELEN, 1975).

$$LOI = 17.5 + 0.4\ (CY) \qquad \text{(Equation 2)}$$

The correlation of LOI values and *CY* has been used extensively (DENG et al., 2017; DUMAS et al., 2016c; FU et al., 2016; KALIAVARADHAN; MUTHUSAMY, 2016; MALLAKPOUR; ZADEHNAZARI, 2017; THIRUKUMARAN et al., 2014) and this method is convenient when the amount of the available samples are highly limited. The LOI values of these polybenzoxazines indicate that these halogen-, silane- and phosphorous-free materials possess outstanding flame retardancy, as polymers containing *LOI* values > 28 are considered as self-extinguishing (MALLAKPOUR; ZADEHNAZARI, 2017). The flame retardancy of these polybenzoxazines showed to be superior than polybenzoxazine of the commercially available **BA-a**, which possesses a *LOI* value of 30.3 (SPONTÓN et al., 2008) and also superior than polyepoxy of the commercially available DGEBA epoxy resin, which possesses *LOI* values around 20.5 to 24.6 (BERESKA et al., 2017; FANG et al., 2017; SHABESTARI et al., 2017).

The mechanical properties of the polybenzoxazines were evaluated by DMA to assess the effect of the different compositions of benzoxazine monomers (**CT-fu** and **BA-fu**) in dynamic mechanical properties against temperature. The DMA curves of the storage modulus (*E'*) and the damping factor (*tan δ*) as a function of the temperature of the polybenzoxazines are shown in Figure 25 and their data are summarized in Table 4.

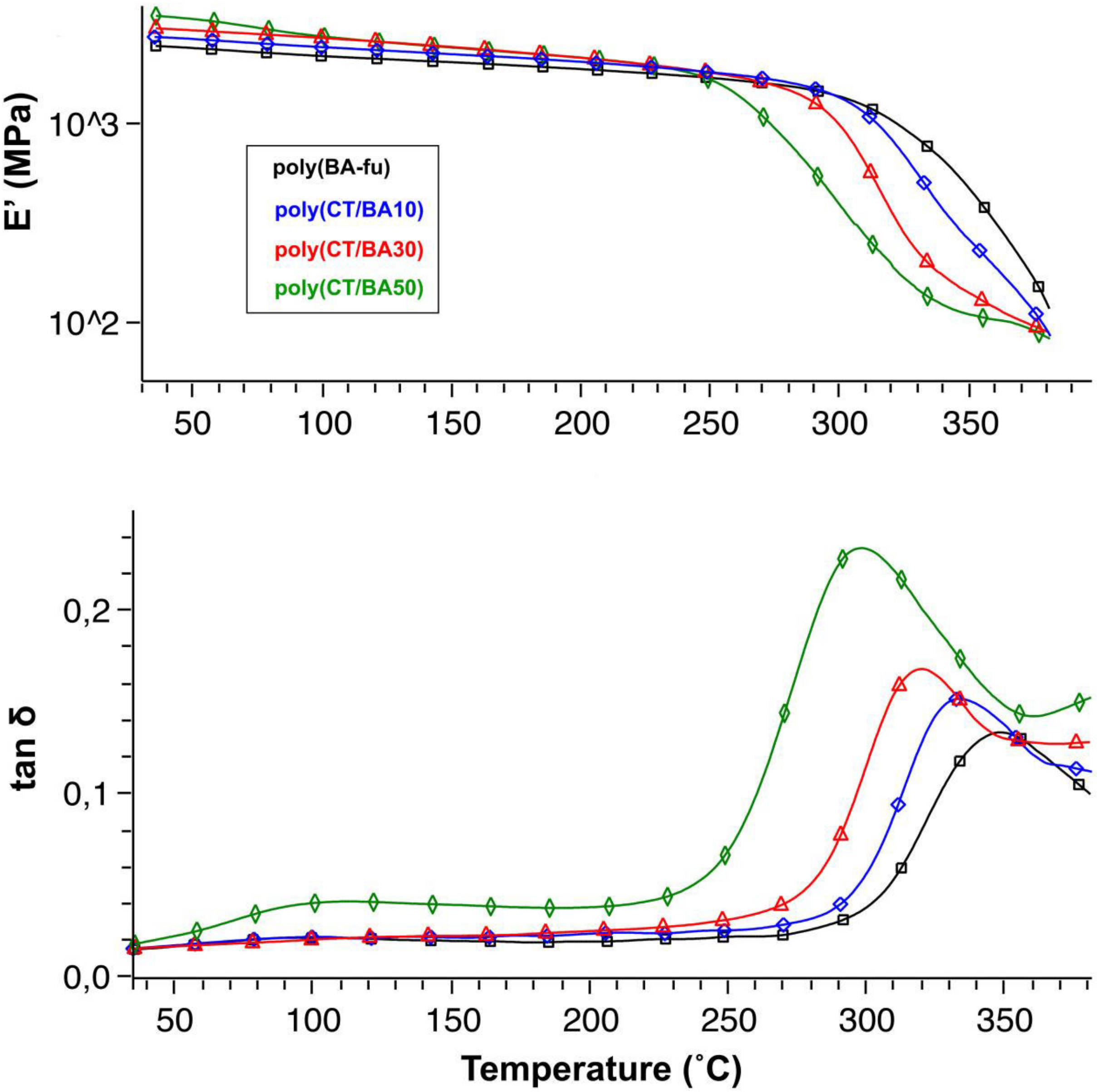
The use of **CT-fu** as a co-monomer demonstrated a significant improvement on the storage modulus of the polybenzoxazines, starting from 2.4 GPa of **poly(BA-fu)** to 3.5 GPa of **poly(CT/BA50)** at 30ºC. Along the entire glassy state, the copolymers also demonstrated superior storage modulus than the homopolymer. At 300ºC the storage modulus of **poly(BA-fu)** and **poly(CT/BA10)** demonstrated to be higher than 1 GPa, indicating that these materials possess reasonably high cross-link density (LIN et al., 2017). On the other hand, by analyzing the *E*' at the same temperature as the other polybenzoxazines, it was noticed that the cross-link densities of the copolymers tended to be lower as the **CT-fu** content increased.

Reduction in the glass transition temperature (T_g), determined as the temperature at the tan δ peak, was observed as **CT-fu** content increased. Somehow, the incorporation of **CT-fu** into the polymeric matrix disrupted the polymer network, changing the molecular structure and increasing the mobility of polymer chains, impairing the mechanical properties.

From the DMA results, it is also possible to correlate T_g and *E'* with the **CT-fu** concentration, as plotted in Figure 26. This observation could indicate a good reliability on the homogenous distributions of the **CT-fu/BA-fu** units in the polymer matrices, suggesting a good processability and compatibility of the monomer mixtures. The height of tan δ peak can be interpreted as the extent of mobility of the polymeric segments at a determined temperature (HILL et al., 2000). As observed in Figure 25, increased amounts of **CT-fu** caused an increase in the tan δ peak, indicating higher energy loss and a more viscous behavior (KALIAVARADHAN; MUTHUSAMY, 2016). All the copolymers showed higher tan δ peak heights than that of the homopolymer. Since an increase in cross-link density typically results in an enhancement of the mechanical properties with the restricted mobility of the polymeric matrix, it was expected that the increase of **CT-fu** content could provide higher cross-link densities on the copolymers, since more reactive furfuryl moieties (mols per mass of monomers) would be available (FROIMOWICZ et al., 2016). However, further investigation is required to a better understand why the increase of **CT-fu** units in the polymer increases significantly the *E*' of the polybenzoxazines at lower temperatures but impairs the thermomechanical stability of the polymers at higher temperatures.

Nevertheless, these (co)polymers are very promising as high-performance materials due to their elevated thermal stabilities, high storage moduli and high T_g, which can reach temperatures up to 300 °C.

Figure 25 - DMA curves of poly(BA-fu), poly(CT/BA10), poly(CT/BA30) and poly(CT/BA50).



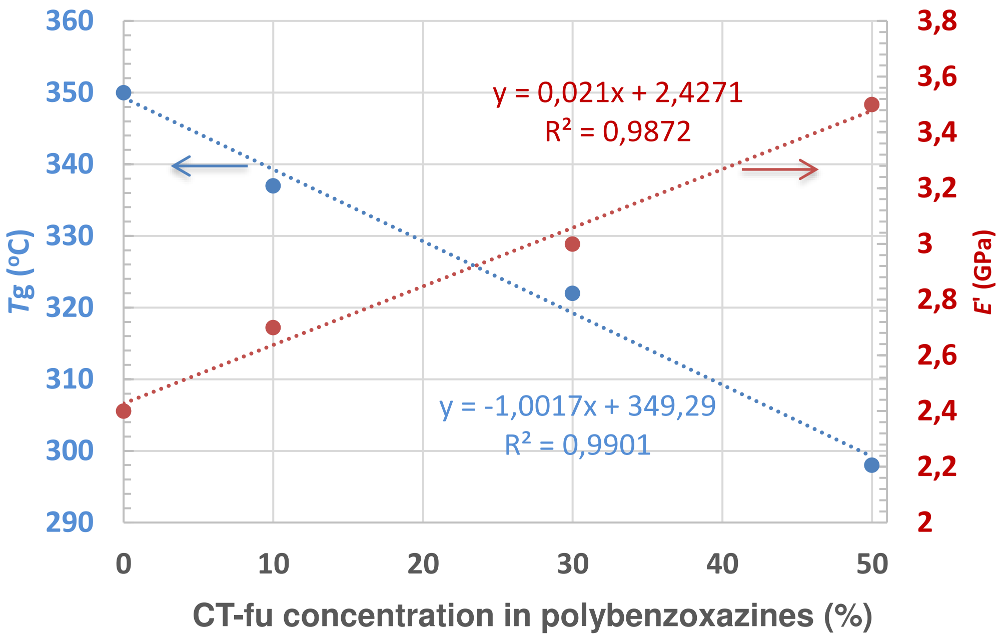
Source: The author

Table 4 - Data of DMA curves of poly(BA-fu), poly(CT/BA10), poly(CT/BA30) and poly(CT/BA50).

Sample	*E'* at 30 °C (GPa)	*E'* at 200 °C (GPa)	*E'* at 300 °C (GPa)	T_g (°C)	tan δ height
Poly(BA-fu)	2.4	1.8	1.3	350	0.13
poly(CT/BA10)	2.7	2.0	1.3	337	0.15
poly(CT/BA30)	3.0	2.1	1.0	322	0.16
poly(CT/BA50)	3.5	2.1	0.4	298	0.23

Source: The author

Figure 26 - Linear correlations of T_g and *E'* with **CT-fu** concentrations



Source: The author

Conclusions

The results presented here suggest that the synthesis of a fully bio-based benzoxazine starting from the lignocellulose-derived products, catechol and furfurylamine, is a valuable tool for the sustainable development of bis-benzoxazine resins. Microwave irradiation along with poly(ethylene glycol) allowed the successful synthesis of thermosetting resins in a matter of few minutes and without the use of toxic chemicals in good yields. Nevertheless, further investigation is being carried out looking forward to the production of benzoxazine resins in larger scales and the effective reuse of PEG. The incorporation of **CT-fu** into **BA-fu** produced high-performance polybenzoxazines with elevated bio-based contents. This novel fully bio-based monomer was also responsible for the incredible *LOI* value presented by **poly(CT/BA50)**, replacing 50% (w/w) of **BA-fu** and giving a copolymer with attractive flame retardant properties.

In this work, we also attempted to demonstrate that lignocellulosic biomass represents a valuable renewable feedstock for the development of highly bio-based derived benzoxazine resins, which can be turned into high-performance thermoset materials.

REFERENCES

A. ATTANASI, O. et al. Solvent Free Synthesis of Novel Mono- and Bis-Benzoxazines from Cashew Nut Shell Liquid Components. **Current Organic Chemistry**, v. 16, n. 21, p. 2613–2621, 1 nov. 2012.

AGAG, T.; JIN, L.; ISHIDA, H. A new synthetic approach for difficult benzoxazines: Preparation and polymerization of 4,4′-diaminodiphenyl sulfone-based benzoxazine monomer. **Polymer**, v. 50, n. 25, p. 5940–5944, nov. 2009.

AHMAD, F.; SILVA, E. L.; VARESCHE, M. B. A. Hydrothermal processing of biomass for anaerobic digestion – A review. **Renewable and Sustainable Energy Reviews**, v. 98, n. December 2017, p. 108–124, 2018.

ALTIN KARATAŞ, M.; GÖKKAYA, H. A review on machinability of carbon fiber reinforced polymer (CFRP) and glass fiber reinforced polymer (GFRP) composite materials. **Defence Technology**, v. 14, n. 4, p. 318–326, ago. 2018.

AMARNATH, N.; APPAVOO, D.; LOCHAB, B. Eco-Friendly Halogen-Free Flame Retardant Cardanol Polyphosphazene Polybenzoxazine Networks. **ACS Sustainable Chemistry & Engineering**, v. 6, n. 1, p. 389–402, 2 jan. 2018.

AMBROŽIČ, R.; ŠEBENIK, U.; KRAJNC, M. Synthesis, curing kinetics, thermal and mechanical behavior of novel cardanol-based benzoxazines. **Polymer**, v. 76, p. 203–212, out. 2015.

ANASTAS, P. T.; WARNER, J. C. **Green Chemistry: Theory and Practice**. New York: Oxford University Press, 1998.

BARANEK, A. D. et al. Flexible aliphatic-bridged bisphenol-based polybenzoxazines. **Polymer Chemistry**, v. 3, n. 10, p. 2892–2900, 2012.

BECKHAM, G. T. et al. Opportunities and challenges in biological lignin valorization. **Current Opinion in Biotechnology**, v. 42, n. March, p. 40–53, dez. 2016.

BERESKA, A. et al. The application of organophosphorus flame-retardants in epoxy resin. **Journal of Vinyl and Additive Technology**, v. 23, n. 2, p. 142–151, maio 2017.

BILAL, M. et al. Biotransformation of lignocellulosic materials into value-added products—A review. **International Journal of Biological Macromolecules**, v. 98, p. 447–458, 2017.

BOBADE, S. K. et al. Bio-Based Thermosetting Resins for Future Generation: A Review. **Polymer-Plastics Technology and Engineering**, v. 55, n. 17, p. 1863–1896, 2016.

BOMTEMPO, J.-V.; CHAVES ALVES, F.; DE ALMEIDA OROSKI, F. Developing new platform chemicals: what is required for a new bio-based molecule to become a platform

chemical in the bioeconomy? **Faraday Discuss.**, v. 202, p. 213–225, 2017.

BRADY, J. et al. Developing Solid Oral Dosage Forms. In: QIU, Y. et al. (Eds.). . 2nd. ed. [s.l.] Academic Press, 2017. p. 1176.

BROWN, E. A.; RIDER, D. A. Pegylated Polybenzoxazine Networks with Increased Thermal Stability from Miscible Blends of Tosylated Poly(ethylene glycol) and a Benzoxazine Monomer. **Macromolecules**, v. 50, n. 17, p. 6468–6481, 2017.

BURKE, W. J. 3,4-Dihydro-1,3,2H-Benzoxazines. Reaction of p -Substituted Phenols with N,N-Dimethylolamines. **Journal of the American Chemical Society**, v. 71, n. 2, p. 609–612, fev. 1949.

BURKE, W. J. et al. A New Aminoalkylation Reaction. Condensation of Phenols with Dihydro-1,3-aroxazines. **The Journal of Organic Chemistry**, v. 30, n. 10, p. 3423–3427, 1965.

BURKE, W. J.; GLENNIE, E. L. M.; WEATHERBEE, C. Condensation of Halophenols with Formaldehyde and Primary Amines. **The Journal of Organic Chemistry**, v. 29, n. 4, p. 909–912, 1964.

BURKE, W. J.; MURDOCK, K. C.; EC, G. Condensation of Hydroxyaromatic Compounds with Formaldehyde and Primary Aromatic Amines. **Journal of the American Chemical Society**, v. 76, n. 6, p. 1677–1679, 1954.

BURKE, W. J.; SMITH, R. P.; WEATHERBEE, C. N,N-Bis-(hydroxybenzyl)-amines: Synthesis from Phenols, Formaldehyde and Primary Amines. **Journal of the American Chemical Society**, v. 74, n. 3, p. 602–605, 1952.

BURKE, W. J.; STEPHENS, C. W. Monomeric Products from the Condensation of Phenol with Formaldehyde and Primary Amines. **Journal of the American Chemical Society**, v. 74, n. 6, p. 1518–1520, mar. 1952.

BURKE, W. J.; WEATHERBEE, C. 3,4-Dihydro-1,3,2H-Benzoxazines. Reaction of Polyhydroxybenzenes with N-Methylolamines 1. **Journal of the American Chemical Society**, v. 72, n. 10, p. 4691–4694, out. 1950.

CALÒ, E. et al. Synthesis of a novel cardanol-based benzoxazine monomer and environmentally sustainable production of polymers and bio-composites. **Green Chemistry**, v. 9, n. 7, p. 754–759, 2007.

CHEN, J. et al. Polyethylene glycol and solutions of polyethylene glycol as green reaction media. **Green Chemistry**, v. 7, n. 2, p. 64–82, 2005.

CHEN, Z.; WAN, C. Biological valorization strategies for converting lignin into fuels and chemicals. **Renewable and Sustainable Energy Reviews**, v. 73, p. 610–621, jun. 2017.

CHIU, W.-M. et al. Preparation and characterization of novel polybenzoxazine hybrid materials.

High Performance Polymers, v. 28, n. 8, p. 971–983, 2016.

CHOI, S.-W. et al. Synthesis, characterization and thermal degradation of functional benzoxazine monomers and polymers containing phenylphosphine oxide. **Polymer Degradation and Stability**, v. 91, n. 5, p. 1166–1178, maio 2006.

CINI, E.; PETRICCI, E.; TADDEI, M. Pd/C Catalysis under Microwave Dielectric Heating. **Catalysts**, v. 7, n. 12, p. 89, 20 mar. 2017.

DAI, J. et al. Biobased Benzoxazine Derived from Daidzein and Furfurylamine: Microwave-Assisted Synthesis and Thermal Properties Investigation. **ChemSusChem**, v. 11, n. 18, p. 3175–3183, 21 set. 2018.

DAYO, A. Q. et al. Natural hemp fiber reinforced polybenzoxazine composites: Curing behavior, mechanical and thermal properties. **Composites Science and Technology**, v. 144, p. 114–124, maio 2017.

DE LEON, A. C. et al. High performance polymer nanocomposites for additive manufacturing applications. **Reactive and Functional Polymers**, v. 103, p. 141–155, jun. 2016.

DENG, C. et al. Modes of action of a mono-component intumescent flame retardant MAPP in polyethylene-octene elastomer. **Polymer Degradation and Stability**, v. 138, p. 142–150, 2017.

DOUSE, E. et al. Modification of stress-strain behaviour in aromatic polybenzoxazines using core shell rubbers. **Reactive and Functional Polymers**, v. 103, p. 117–130, jun. 2016.

DRIOWYA, M. et al. **Microwave-assisted synthesis of bioactive six-membered heterocycles and their fused analogues**. [s.l: s.n.]. v. 21

DUMAS, L. et al. Eugenol-based benzoxazine: from straight synthesis to taming of the network properties. **J. Mater. Chem. A**, v. 3, n. 11, p. 6012–6018, 2015.

DUMAS, L. et al. Arbutin-based benzoxazine: en route to an intrinsic water soluble biobased resin. **Green Chem.**, v. 18, n. 18, p. 4954–4960, 2016a.

DUMAS, L. et al. High performance bio-based benzoxazine networks from resorcinol and hydroquinone. **European Polymer Journal**, v. 75, p. 486–494, fev. 2016b.

DUMAS, L. et al. Chavicol benzoxazine: Ultrahigh Tg biobased thermoset with tunable extended network. **European Polymer Journal**, v. 81, p. 337–346, ago. 2016c.

ERDOCIA, X. et al. Base catalyzed depolymerization of lignin: Influence of organosolv lignin nature. **Biomass and Bioenergy**, v. 66, p. 379–386, jul. 2014.

FANG, Y. et al. Flame retardant performance of a carbon source containing DOPO derivative in PET and epoxy. **Journal of Applied Polymer Science**, v. 134, n. 12, p. 1–9, 2017.

FAO. **FAO**. Disponível em: http://faostat3.fao.org/faostat-gateway/go/to/browse/Q/QC/E. Acesso em: 28 set. 2018.

FERNÁNDEZ-RODRÍGUEZ, J. et al. Lignin depolymerization for phenolic monomers production by sustainable processes. **Journal of Energy Chemistry**, v. 26, n. 4, p. 622–631, jul. 2017.

FROIMOWICZ, P. et al. Smart, Sustainable, and Ecofriendly Chemical Design of Fully Bio-Based Thermally Stable Thermosets Based on Benzoxazine Chemistry. **ChemSusChem**, v. 9, n. 15, p. 1921–1928, 9 ago. 2016.

FROIMOWICZ, P.; ZHANG, K.; ISHIDA, H. Intramolecular Hydrogen Bonding in Benzoxazines: When Structural Design Becomes Functional. **Chemistry - A European Journal**, v. 22, n. 8, p. 2691–2707, 2016.

FU, T. et al. Inherent flame retardation of semi-aromatic polyesters via binding small-molecule free radicals and charring. **Polymer Chemistry**, v. 7, n. 8, p. 1584–1592, 2016.

GRAMEC SKLEDAR, D.; PETERLIN MAŠIČ, L. Bisphenol A and its analogs: Do their metabolites have endocrine activity? **Environmental Toxicology and Pharmacology**, v. 47, p. 182–199, out. 2016.

HAN, L. et al. Oxazine Ring-Related Vibrational Modes of Benzoxazine Monomers Using Fully Aromatically Substituted, Deuterated, 15 N Isotope Exchanged, and Oxazine-Ring-Substituted Compounds and Theoretical Calculations. **The Journal of Physical Chemistry A**, v. 121, n. 33, p. 6269–6282, 24 ago. 2017.

HARRIS, J. M. (ED.). Poly(Ethylene Glycol) Chemistry. In: **Biotechnical and Biomedical Applications**. Boston, MA: Springer US, 1992.

HASSAN, W. A. W. et al. Examining the influence of bisphenol A on the polymerisation and network properties of an aromatic benzoxazine. **Polymer**, v. 88, p. 52–62, 2016.

HILL, D. J. T. et al. Dynamic mechanical properties of networks prepared from siloxane modified divinyl benzene pre-polymers. **Polymer**, v. 41, n. 26, p. 9131–9137, dez. 2000.

HOLLY, F. W.; COPE, A. C. Condensation Products of Aldehydes and Ketones with o-Aminobenzyl Alcohol and o-Hydroxybenzylamine. **Journal of the American Chemical Society**, v. 66, n. 11, p. 1875–1879, nov. 1944.

HÜLSEY, M. J.; YANG, H.; YAN, N. Sustainable Routes for the Synthesis of Renewable Heteroatom-Containing Chemicals. **ACS Sustainable Chemistry & Engineering**, v. 6, n. 5, p. 5694–5707, 7 maio 2018.

HUNTSMAN. **Benzoxazines**. Disponível em: http://www.huntsman.com/advanced_materials/a/Our Technologies/High Performance Components/Imides and Benzoxazines/Benzoxazines. Acesso em: 22 set. 2018.

IREDALE, R. J.; WARD, C.; HAMERTON, I. Modern advances in bismaleimide resin technology: A 21st century perspective on the chemistry of addition polyimides. **Progress in Polymer Science**, v. 69, p. 1–21, jun. 2017.

ISHIDA, H.; AGAG, T. Handbook of Benzoxazine Resins. In: ISHIDA, H.; AGAG, T. (Eds.). . **Handbook of Benzoxazine Resins**. Oxford: Elsevier, 2011. p. 712.

ISHIDA, H.; SANDERS, D. P. Improved Thermal and Mechanical Properties of Polybenzoxazines Based on Alkyl-Substituted Aromatic Amines. **Polymer**, v. 38, p. 3289–3301, 2000.

ISIKGOR, F. H.; BECER, C. R. Lignocellulosic biomass: a sustainable platform for the production of bio-based chemicals and polymers. **Polymer Chemistry**, v. 6, n. 25, p. 4497–4559, 2015.

JEENPADIPHAT, S.; MONGKOLPICHAYARAK, I.; TUNGASMITA, D. N. Catechol production from lignin by Al-doped mesoporous silica catalytic cracking. **Journal of Analytical and Applied Pyrolysis**, v. 121, p. 318–328, set. 2016.

KALIAVARADHAN, K.; MUTHUSAMY, S. Synthesis and characterization of various phenylene diamine-based bismaleimide-containing phthalonitrile resins. **Polymer Bulletin**, v. 73, n. 7, p. 1921–1938, 2016.

KAPPE, C. O. Controlled Microwave Heating in Modern Organic Synthesis. **Angewandte Chemie International Edition**, v. 43, n. 46, p. 6250–6284, 26 nov. 2004.

KATHALEWAR, M.; SABNIS, A.; D'MELO, D. Polyurethane coatings prepared from CNSL based polyols: Synthesis, characterization and properties. **Progress in Organic Coatings**, v. 77, n. 3, p. 616–626, 2014.

KHAN, M. A. et al. Experimental and numerical analysis of flexural and impact behaviour of glass/pp sandwich panel for automotive structural applications. **Advanced Composite Materials**, v. 27, n. 4, p. 367–386, 4 jul. 2018.

KISKAN, B.; GHOSH, N. N.; YAGCI, Y. Polybenzoxazine-based composites as high-performance materials. **Polymer International**, v. 60, n. 2, p. 167–177, fev. 2011.

KOPSIDAS, S.; HAMERTON, I. Examining the thermal behaviour of novel aromatic polybenzoxazine blends containing an organophosphorous compound and polyhedral oligomeric silsesquioxane reagents. **Polymer International**, v. 65, n. 9, p. 1015–1023, set. 2016.

KOTZEBUE, L. R. V. et al. Spectral and thermal studies on the synthesis and catalyzed oligomerization of novel cardanol-based benzoxazines. **Polymer**, v. 92, p. 189–200, 2016.

KOTZEBUE, L. R. V. et al. Development of Fully Biobased High-Performance Bis-Benzoxazine under Environmentally Friendly Conditions. **ACS Sustainable Chemistry & Engineering**, v. 6, n. 4, p. 5485–5494, 2018.

LAURICHESSE, S.; AVÉROUS, L. Chemical modification of lignins: Towards biobased polymers. **Progress in Polymer Science**, v. 39, n. 7, p. 1266–1290, 2014.

LI, B. et al. Preparation of bio-based phenol formaldehyde foams using depolymerized hydrolysis lignin. **Industrial Crops and Products**, v. 97, p. 409–416, mar. 2017.

LI, W. et al. Preparation of novel benzoxazine monomers containing ferrocene moiety and properties of polybenzoxazines. **Polymer**, v. 53, n. 6, p. 1236–1244, 2012.

LIN, C. H. et al. Synthesis of a Bisbenzylideneacetone-Containing Benzoxazine and Its Photo- and Thermally Cured Thermoset. **ACS Omega**, v. 2, n. 7, p. 3432–3440, 2017.

LIU, Y.-L.; CHOU, C.-I. High performance benzoxazine monomers and polymers containing furan groups. **Journal of Polymer Science Part A: Polymer Chemistry**, v. 43, n. 21, p. 5267–5282, 2005.

LLIGADAS, G. et al. Polybenzoxazines: new players in the bio-based polymer arena. **Polym. Chem.**, v. 5, n. 23, p. 6636–6644, 2014.

LOCHAB, B.; VARMA, I. K.; BIJWE, J. Thermal behaviour of cardanol-based benzoxazines. **Journal of Thermal Analysis and Calorimetry**, v. 102, n. 2, p. 769–774, 9 nov. 2010.

LOCHAB, B.; VARMA, I. K.; BIJWE, J. Cardanol-based bisbenzoxazines. **Journal of Thermal Analysis and Calorimetry**, v. 107, n. 2, p. 661–668, 26 ago. 2011.

LOMONACO, D. et al. Thermal studies of new biodiesel antioxidants synthesized from a natural occurring phenolic lipid. **Fuel**, v. 97, p. 552–559, jul. 2012.

LOMONACO, D.; MELE, G.; MAZZETTO, S. E. Cashew Nutshell Liquid (CNSL): From an Agro-industrial Waste to a Sustainable Alternative to Petrochemical Resources. In: ANILKUMAR, P. (Ed.). . **Cashew Nut Shell Liquid**. Zurich: Springer, Cham, 2017. p. 19–38.

MA, R.; GUO, M.; ZHANG, X. Recent advances in oxidative valorization of lignin. **Catalysis Today**, v. 302, p. 50–60, 2018.

MALLAKPOUR, S.; ZADEHNAZARI, A. Improved covalent functionalization of multi-walled carbon nanotubes using ascorbic acid for poly(amide–imide) composites having dopamine linkages. **Bulletin of Materials Science**, v. 40, n. 1, p. 213–222, 2017.

MALLOZZI, M. et al. Endocrine Disrupting Chemicals and Endometrial Cancer: An Overview of Recent Laboratory Evidence and Epidemiological Studies. **International Journal of Environmental Research and Public Health**, v. 14, n. 3, p. 334, 2017.

MAMANPUSH, S. H. et al. Recycled wind turbine blades as a feedstock for second generation composites. **Waste Management**, v. 76, p. 708–714, jun. 2018.

MANIKANNAN, R.; MUTHUSUBRAMANIAN, S. Synthesis and biological activity of 6-

alkyl/chloro-3-{4-(6-alkyl/chloro-2H-benzo[e][1,3]oxazin-3(4H)-yl}-3,4-dihydro-2H-benzo[e][1,3]oxazines. **Indian Journal of Chemistry**, v. 49B, n. August, p. 1083–1087, 2010.

MARTINEZ, C. R.; IVERSON, B. L. Rethinking the term “pi-stacking”. **Chemical Science**, v. 3, n. 7, p. 2191–2201, 2012.

MAZZETTO, S. E.; LOMONACO, D. Cashew nut oil: opportunities and challenges in the context of sustainable industrial. **Quimica Nova**, v. 32, n. 3, p. 732–741, 2009.

MENARD, K. P. DYNAMIC MECHANICAL ANALYSIS - A Practical Introduction. In: Boca Raton: CRC Press, 1999. p. 240.

MONISHA, M. et al. Cardanol Benzoxazines: A Versatile Monomer with Advancing Applications. **Macromolecular Chemistry and Physics**, v. 220, n. 3, p. 1800470, 11 fev. 2019.

MOVIL-CABRERA, O. et al. Electrochemical conversion of lignin to useful chemicals. **Biomass and Bioenergy**, v. 88, p. 89–96, maio 2016.

NATARAJAN, M.; MURUGAVEL, S. C. Synthesis, spectral and thermal degradation kinetics of novolac resins derived from cardanol. **High Performance Polymers**, v. 25, n. 6, p. 685–696, 2013.

NG, F. et al. Bio-Based Aromatic Epoxy Monomers for Thermoset Materials. **Molecules**, v. 22, n. 1, p. 149, 18 jan. 2017.

NIELSEN, L. E. Cross-Linking–Effect on Physical Properties of Polymers. **Journal of Macromolecular Science, Part C**, v. 3, n. 1, p. 69–103, 10 jan. 1969.

NING, X.; ISHIDA, H. Phenolic materials via ring-opening polymerization of benzoxazines: Effect of molecular structure on mechanical and dynamic mechanical properties. **Journal of Polymer Science Part B: Polymer Physics**, v. 32, n. 5, p. 921–927, 15 abr. 1994a.

NING, X.; ISHIDA, H. Phenolic materials via ring-opening polymerization: Synthesis and characterization of bisphenol-A based benzoxazines and their polymers. **Journal of Polymer Science Part A: Polymer Chemistry**, v. 32, n. 6, p. 1121–1129, 30 abr. 1994b.

ODIAN, G. **Principles of Polymerization**. 4th. ed. New Jersey: Wiley-Interscience, 2004.

OLIVEIRA, J. R. et al. Microwave-assisted solvent-free synthesis of novel benzoxazines: A faster and environmentally friendly route to the development of bio-based thermosetting resins. **Journal of Polymer Science Part A: Polymer Chemistry**, v. 55, n. 21, p. 3534–3544, 1 nov. 2017.

PERIYASAMY, T.; ASRAFALI, S. P.; KIM, S.-C. Functionalized MWCNTs, an efficient reinforcement for the preparation of eugenol based high performance PBz/BMI/CNT nanocomposites exhibiting outstanding thermo-mechanical properties. **New Journal of Chemistry**, v. 41, n. 14, p. 6607–6615, 2017.

PHALAK, G. A.; PATIL, D. M.; MHASKE, S. T. Synthesis and characterization of thermally curable guaiacol based poly(benzoxazine-urethane) coating for corrosion protection on mild steel. **European Polymer Journal**, v. 88, p. 93–108, mar. 2017.

RAQUEZ, J.-M. et al. Thermosetting (bio)materials derived from renewable resources: A critical review. **Progress in Polymer Science**, v. 35, n. 4, p. 487–509, abr. 2010.

REISS, G. et al. **Advances in Polymer Synthesis**. New York: Springer US, 1985.

RIBEIRO, F. W. M. et al. Thermal and mechanical analyses of biocomposites from cardanol-based polybenzoxazine and bamboo fibers. **Journal of Thermal Analysis and Calorimetry**, v. 129, n. 1, p. 281–289, 21 jul. 2017.

RODRÍGUEZ, A. M. et al. Influence of Polarity and Activation Energy in Microwave-Assisted Organic Synthesis (MAOS). **ChemistryOpen**, v. 4, n. 3, p. 308–317, jun. 2015.

RUČIGAJ, A.; GRADIŠAR, Š.; KRAJNC, M. Kinetic investigation of a complex curing of the guaiacol bio-based benzoxazine system. **E-Polymers**, v. 16, n. 3, p. 199–206, 2016.

SAHOO, S.; MOHANTY, S.; NAYAK, S. K. Biobased polyurethane adhesive over petroleum based adhesive: Use of renewable resource. **Journal of Macromolecular Science, Part A**, v. 55, n. 1, p. 36–48, 2018.

SAINI, N. K.; AZECHI, M.; ENDO, T. Synthesis and Properties of Spiro-Centered Benzoxazines. **Macromolecules**, v. 48, n. 20, p. 7466–7472, 2015.

SHABESTARI, M. E. et al. Effect of nitrogen and oxygen doped carbon nanotubes on flammability of epoxy nanocomposites. **Carbon**, v. 121, p. 193–200, 2017.

SHARMA, V. et al. Benzoxazine derivatives of phytophenols show anti-plasmodial activity via sodium homeostasis disruption. **Bioorganic & Medicinal Chemistry Letters**, mar. 2018.

SHELDON, R. A. Organic Synthesis - Past, Present and Future. **Chemistry & Industry (London)**, p. 903–906, 1992.

SHELDON, R. A. The E factor 25 years on: the rise of green chemistry and sustainability. **Green Chemistry**, v. 19, n. 1, p. 18–43, 2017.

SHELDON, R. A. Metrics of Green Chemistry and Sustainability: Past, Present, and Future. **ACS Sustainable Chemistry & Engineering**, v. 6, n. 1, p. 32–48, 2 jan. 2018a.

SHELDON, R. A. The Road to Biorenewables: Carbohydrates to Commodity Chemicals. **ACS Sustainable Chemistry & Engineering**, v. 6, n. 4, p. 4464–4480, 2 abr. 2018b.

SHEN, S. B.; ISHIDA, H. Synthesis and characterization of polyfunctional naphthoxazines and related polymers. **Journal of Applied Polymer Science**, v. 61, n. 9, p. 1595–1605, 29 ago. 1996.

SHIKOKU. **Benzoxazine**. Disponível em: http://www.shikoku.co.jp/eng/products/chemical/fine-chemical/benzoxazine.php. Acesso em: 25 set. 2018.

SHUKLA, S. et al. Cardanol benzoxazines – interplay of oxazine functionality (mono to tetra) and properties. **RSC Advances**, v. 5, n. 95, p. 78071–78080, 2015.

SINI, N. K.; BIJWE, J.; VARMA, I. K. Renewable benzoxazine monomer from Vanillin: Synthesis, characterization, and studies on curing behavior. **Journal of Polymer Science, Part A: Polymer Chemistry**, v. 52, n. 1, p. 7–11, 2014.

SOMISETTI, V. et al. Flexible, hard, and tough biobased polyurethane thermosets from renewable materials: glycerol and 10-undecenoic acid. **Journal of Coatings Technology and Research**, v. 15, n. 1, p. 199–210, 2018.

SPONTÓN, M. et al. Studies on thermal and flame retardant behaviour of mixtures of bis(m-aminophenyl)methylphosphine oxide based benzoxazine and glycidylether or benzoxazine of Bisphenol A. **Polymer Degradation and Stability**, v. 93, n. 12, p. 2158–2165, 2008.

TAKEICHI, T.; KAWAUCHI, T.; AGAG, T. High Performance Polybenzoxazines as a Novel Type of Phenolic Resin. **Polymer Journal**, v. 40, n. 12, p. 1121–1131, 15 dez. 2008.

TEONG, S. P.; YI, G.; ZHANG, Y. Hydroxymethylfurfural production from bioresources: past, present and future. **Green Chemistry**, v. 16, n. 4, p. 2015–2026, 2014.

THIRUKUMARAN, P. et al. Synthesis and characterization of new polybenzoxazines from renewable resources for bio-composite applications. **Polymer Composites**, v. 16, n. 2, p. 1–9, 2014.

TRAN, P.; NGUYEN, Q. T.; LAU, K. T. Fire performance of polymer-based composites for maritime infrastructure. **Composites Part B: Engineering**, v. 155, n. June, p. 31–48, dez. 2018.

TREJO-MACHIN, A. et al. Phloretic acid as an alternative to the phenolation of aliphatic hydroxyls for the elaboration of polybenzoxazine. **Green Chem.**, v. 19, n. 21, p. 5065–5073, 2017.

TRITA, A. S. et al. Synthesis of potential bisphenol A substitutes by isomerising metathesis of renewable raw materials. **Green Chem.**, v. 19, n. 13, p. 3051–3060, 2017.

TROST, B. M. The atom economy - a search for synthetic efficiency. **Science**, v. 254, n. 5037, p. 1471–1477, 1991.

VAFAEEZADEH, M.; HASHEMI, M. M. Polyethylene glycol (PEG) as a green solvent for carbon-carbon bond formation reactions. **Journal of Molecular Liquids**, v. 207, p. 73–79, 2015.

VAN GEMERT, D. et al. Cement concrete and concrete–polymer composites: Two merging worlds. **Cement and Concrete Composites**, v. 27, n. 9–10, p. 926–933, out. 2005.

VAN KREVELEN, D. . Some basic aspects of flame resistance of polymeric materials. **Polymer**, v. 16, n. 8, p. 615–620, ago. 1975.

VINITA, Y. **Yamamoto Vinita**. Disponível em: http://www.vinita.co.jp/en/advanced/technical_information/principle.html. Acesso em: 3 out. 2018.

VOIRIN, C. et al. Functionalization of cardanol: towards biobased polymers and additives. **Polym. Chem.**, v. 5, n. 9, p. 3142–3162, 2014.

WAHYUDIONO; SASAKI, M.; GOTO, M. Recovery of phenolic compounds through the decomposition of lignin in near and supercritical water. **Chemical Engineering and Processing: Process Intensification**, v. 47, n. 9–10, p. 1609–1619, set. 2008.

WANG, C.-F. et al. Low-Surface-Free-Energy Materials Based on Polybenzoxazines. **Angewandte Chemie International Edition**, v. 45, n. 14, p. 2248–2251, 27 mar. 2006a.

WANG, C.-F. et al. Stable Superhydrophobic Polybenzoxazine Surfaces over a Wide pH Range. **Langmuir**, v. 22, n. 20, p. 8289–8292, set. 2006b.

WANG, C. et al. Synthesis and copolymerization of fully bio-based benzoxazines from guaiacol, furfurylamine and stearylamine. **Green Chemistry**, v. 14, n. 10, p. 2799–2806, 2012.

WANG, Y.-X.; ISHIDA, H. Synthesis and Properties of New Thermoplastic Polymers from Substituted 3,4-Dihydro-2 H -1,3-benzoxazines. **Macromolecules**, v. 33, n. 8, p. 2839–2847, abr. 2000.

WANG, Z.; LIU, H.; LIU, S. Low-Dose Bisphenol A Exposure: A Seemingly Instigating Carcinogenic Effect on Breast Cancer. **Advanced Science**, v. 4, n. 2, p. 1600248, 2016.

WENDISCH, V. F.; KIM, Y.; LEE, J.-H. Chemicals from lignin: Recent depolymerization techniques and upgrading extended pathways. **Current Opinion in Green and Sustainable Chemistry**, v. 14, p. 33–39, 2018.

XU, H. et al. Hybrid polybenzoxazine with tunable properties. **RSC Advances**, v. 3, n. 11, p. 3677, 2013.

ZHANG, H. et al. Preparation of superhydrophobic polybenzoxazine/SiO2 films with self-cleaning and ice delay properties. **Progress in Organic Coatings**, v. 123, n. January, p. 254–260, out. 2018.

ZHANG, J. et al. Highly efficient, NiAu-catalyzed hydrogenolysis of lignin into phenolic chemicals. **Green Chem.**, v. 16, n. 5, p. 2432–2437, 2014.

ZHANG, L. et al. Cardanol-capped main-chain benzoxazine oligomers for resin transfer molding. **European Polymer Journal**, v. 93, n. June, p. 284–293, ago. 2017.

ZHU, L.; LI, N.; CHILDS, P. R. N. Light-weighting in aerospace component and system design. **Propulsion and Power Research**, v. 7, n. 2, p. 103–119, jun. 2018.

ZIRBES, M.; WALDVOGEL, S. R. Electro-conversion as sustainable method for the fine chemical production from the biopolymer lignin. **Current Opinion in Green and Sustainable Chemistry**, v. 14, p. 19–25, 2018.

4 TOWARDS BIO-BASED HIGH-PERFORMANCE POLYBENZOXAZINES: AGRO-WASTES AS STARTING MATERIALS FOR BPA-FREE THERMOSETS VIA EFFICIENT MICROWAVE-ASSISTED SYNTHESIS

RESUMO

Neste trabalho é descrito o uso do líquido de casca de castanha de caju (CNSL) e o catecol derivado de lignina como materiais de partida renováveis amplamente disponíveis para a síntese de benzoxazinas livres de BPA. As resinas bio-baseadas foram obtidas através de um eficiente método ecologicamente correto, utilizando irradiação de microondas como fonte de calor, produzindo resinas com bons rendimentos. Após caracterização por espectroscopia na região no infravermelho com transformada de Fourier (FTIR), espectroscopia de ressonância magnética nuclear (RMN de 1H e 13C) e calorimetria exploratória diferencial (DSC), estas resinas foram misturadas em diferentes concentrações e foram termicamente (co)polimerizadas para obtenção de polibenzoxazinas totalmente bio-baseadas. Esses termofixas foram estudados por análise termogravimétrica (TGA), análise mecânica dinâmica (DMA) e teste de flexão de três pontos, que mostraram conteúdos de cinzas elevados (até 40%) e boas propriedades mecânicas (Tg acima de 200 °C). Métricas sustentáveis, fator E Economia de átomos, também foram aplicadas para síntese de monômeros renováveis demonstrando quanto sustentáveis estes processos são, sugerindo que estes materiais podem ser considerados alternativas interessantes de alto desempenho para substituir as polibenzoxazinas a base de BPA.

Palavras-chaves: Polibenzoxazinas. Líquido da Casca da Castanha de Caju. Lignina. Métricas Sustentáveis

ABSTRACT

In this work is described the use of Cashew Nut Shell Liquid (CNSL) and the lignin-derivate catechol as widely available renewable starting materials for the synthesis of BPA-free benzoxazines. The bio-based resins were obtained through an efficient eco-friendly method using microwave-irradiation as a heating source, producing resins with good yields. After characterization by Fourier transform infrared spectroscopy (FTIR), nuclear magnetic resonance Spectroscopy (^{1}H and ^{13}C NMR) and differential scanning calorimetry (DSC), these resins were combined in different ratios and then thermally (co)polymerized to obtain fully bio-based polybenzoxazines. These thermosets were studied by thermogravimetric analysis (TGA), dynamic mechanical analysis (DMA) and three-point flexural test, which showed elevated char yield (up to 40%) and good mechanical properties (*Tg* above 200 °C). Sustainable metrics, E factor and Atom Economy, were also applied for the synthesis of the bio-based monomers demonstrating the greenness of this processes and suggesting that these materials can be considered interesting high-performance alternatives to substitute BPA-based polybenzoxazines.

Keywords: Polybenzoxazines. Cashew Nut Shell Liquid. Lignin, Sustainable Metrics

Introduction

The constant search to develop new bio-based polymers is a current trend among the scientists that seek ways to contribute heavily with the circular economy. The growing rigorous laws of environmental agencies and environmental awareness of consumers turned bio-based thermosets as one of the most studied renewable polymers, due to the low cost and the global availability of biomass as starting material, with applications that range from adhesives to high-performance polymers (BOBADE et al., 2016)· The most known bio-based thermosets are phenolics (LI et al., 2017; NATARAJAN; MURUGAVEL, 2013), polyurethanes (KATHALEWAR; SABNIS; D'MELO, 2014; SAHOO; MOHANTY; NAYAK, 2018; SOMISETTI et al., 2018) and epoxies (NG et al., 2017) which use mostly vegetable oils, cardanol and lignin derivates as starting material. But another class of polymers that have entered this field to dispute with these renewable polymers are polybenzoxazines, which are polymeric products of benzoxazines.

Benzoxazines are a class of high performance thermosetting resins that have attracted the attention of industrial and academic sectors due to their peculiar properties, such as: easy thermal curing by ring-opening polymerization, in which the use of catalysts or hardeners is not required, low thermal expansion, high glass transition temperature (T_g), low moisture absorption, good chemical resistance and improved thermal and mechanical properties (DUMAS et al., 2016a; FROIMOWICZ; ZHANG; ISHIDA, 2016; YAGCI; KISKAN; GHOSH, 2009). Another very attractive characteristic from the synthetic point of view is the great molecular design flexibility, since the synthesis of these monomers occurs from a phenolic compound, a primary amine and formaldehyde, making it possible to use a wide variety of starting materials, including derivatives of renewable feedstock (ISHIDA; AGAG, 2011).

Phenolic compounds are described as the most studied starting materials in the literature of benzoxazines. Additionally, one of the richest and natural sources of these compounds is the Cashew Nut Shell Liquid (CNSL), localized in the honeycomb of the cashew nutshell (*Anacardium occidentale L.*) (LOMONACO et al., 2012). The *natural* CNSL possesses a chemical composition of anacardic acid (71.70 – 82.00 %), cardol (13.80 – 20.10 %), cardanol (1.60 – 9.20 %) and 2-methyl cardol (1.65 – 3.90 %) (MAZZETTO; LOMONACO, 2009), but due to the elevated temperatures during the almond processing of the cashew nut industries, the anacardic acid suffers a decarboxylation reaction, turning this CNSL rich in cardanol (LOMONACO et al., 2012). This CNSL, also called as *technical* CNSL, is the main by-product after the industrial processing of the cashew almond and it possesses a chemical composition of cardanol (67.82 – 94.60 %), cardol (3.80 – 18.86 %), anacardic acid (1.09 – 1.75 %), 2-methyl cardol (1.20 – 4.10 %) and polymeric materials (0.34 – 21.63 %) (MAZZETTO; LOMONACO, 2009).

Considering that in 2016 the world production of cashew nuts *in natura* was almost 5 million tons,(FAO, 2018) and knowing that CNSL represents around 25 % in weight of the nut (KOTZEBUE et al., 2016) it can be estimated that around 1.25 million tons of CNSL could be produced on that year. This large quantity of by-product, aligned with the chemical versatility of the phenolic compounds and the low cost, makes CNSL a very promising and renewable raw material for the development of new bio-based benzoxazines (LOMONACO; MELE; MAZZETTO, 2017).

Another interesting agro-industrial waste is lignin, an amorphous heterogeneous macromolecule localized in the cell walls of vascular plants, which its main usage is to provide protection against biochemical interventions by avoiding enzymatic reactions of inner components (LAURICHESSE; AVÉROUS, 2014). Being considered as the second most abundant biopolymer, lignin consists of a complex structure containing mainly three units: guaiacyl (G), *p*-hydroxyphenyl (H) and syringyl (S) (MA; GUO; ZHANG, 2018). According to Laurichesse and Avérous (LAURICHESSE; AVÉROUS, 2014), the global availability of lignin can exceed 300 billion tons and only the pulp and paper industries produced around 50 million tons in 2010. The immense availability of this feedstock has put scientists to dedicate a lot of efforts to depolymerize lignin into phenylpropanoids, as these are considered to be very interesting for the production of a various value-added bio-aromatics such as vanillin, guaiacol and catechol (ERDOCIA et al., 2014; FERNÁNDEZ-RODRÍGUEZ et al., 2017; JEENPADIPHAT; MONGKOLPICHAYARAK; TUNGASMITA, 2016).

Previously, it was demonstrated that catechol is a promising renewable phenolic compound to synthesize bis-benzoxazine (**CT-fu**) making it suitable for producing high thermal and mechanical resistant thermosets with glass transition temperatures (T_g) above 250 ºC (KOTZEBUE et al., 2018).

Benzoxazines synthesized from CNSL-based phenols are reported in the literature and their polymers demonstrated interesting thermal properties (KOTZEBUE et al., 2016; RIBEIRO et al., 2017). However, due to the low values of storage moduli (E') and the low glass transition temperature (T_g), the thermomechanical properties of CNSL-based polybenzoxazines turn them not so desired for high-performance materials (RIBEIRO et al., 2017; SHUKLA et al., 2015). The reason that these polybenzoxazines possess these properties is due to the great mobility of long aliphatic chains of their respective phenols, which suggests a low crosslinking density of the polymer (RIBEIRO et al., 2017; SHUKLA et al., 2015).

A strategy already reported in the literature to improve the mechanical properties and the glass transition temperatures of the cardanol-based polybenzoxazines is the functionalization of the instaurations on the aliphatic chain, such as epoxidation (AMBROŽIČ; ŠEBENIK; KRAJNC, 2015). Ambrožič and coworkers demonstrated that the epoxy-functionalized polybenzoxazine had a storage modulus (in shear mode) almost twice as high as of the conventional cardanol-based polybenzoxazines (AMBROŽIČ; ŠEBENIK; KRAJNC, 2015). On the other hand, the glass transition temperature (T_g) reported did not increase significantly, which was from 89 to 110 ºC (AMBROŽIČ; ŠEBENIK; KRAJNC, 2015). Due to these low T_g and to the reactivity of the epoxy groups, that can react with primary amines during the benzoxazines synthesis, another strategy to increase the thermomechanical properties of CNSL-based polybenzoxazines is still recommended.

An alternative to obtain polybenzoxazine with good thermal and mechanical properties, is by increasing the number of oxazine rings in a monomer, such as bis-benzoxazines, which could increase significantly the crosslinking in the polymer matrix (ISHIDA; AGAG, 2011). As cardanol-based benzoxazines are generally monofunctional, a strategy to use this monomer for high-performance thermosets is its (co)polymerization with a bis-benzoxazine. Kotzebue and co-workers performed a study of copolymerization with catechol- and BPA-based bis-benzoxazines (**CT-fu** and **BA-fu**, respectively) and it was observed that the insertion of **CT-fu** greatly improved the properties of the copolymer (KOTZEBUE et al., 2018).

Therefore, considering the renewability of catechol and furfurylamine (WANG et al., 2013; DUMAS et al., 2016b), the main purpose of this work is to synthesize highly bio-based benzoxazines from non-edible CNSL and improve the thermal and mechanical properties of its polybenzoxazine by copolymerizing it with catechol-based bis-benzoxazine.

After the structural and thermal characterization of benzoxazine monomers obtained by Fourier transform infrared spectroscopy (FTIR), ^{1}H and ^{13}C nuclear magnetic resonance spectroscopy (NMR), and differential scanning calorimetry (DSC), the copolymers were investigated by thermogravimetric analysis (TGA), dynamic (DMA) and static mechanical analysis .

Experimental

Materials

Technical CNSL (Cashew nutshell liquid) was supplied by Amêndoas do Brasil LTDA. Catechol (99%), furfurylamine (99%) and paraformaldehyde (99%) were used as received from Sigma-Aldrich. PEG (Kollisolv® PEG E 400) was used as received from Aldrich. Ethyl acetate, dichloromethane, methanol, sodium hydroxide and anhydrous sodium sulphate, were used as received from LabSynth (Brazil).

Synthesis and analytical methods

Microwave-assisted organic synthesis

The microwave-assisted organic synthesis was performed in a Milestone microwave reactor, model StartSYNTH, operating in an open-vessel configuration at a frequency of 2.45 GHz. The temperature set was controlled by a contact-less infrared sensor, and the power applied was limited to 500 W.

Fourier Transform Infrared Spectroscopy (FTIR)

The FTIR spectra were obtained using a Perkin Elmer FTIR/NIR FRONTIER spectrometer, using attenuated total reflectance (ATR) fixture with zinc selenide crystal surface (ZnSe), and resolution of 4 cm^{-1} using the arithmetic average of 32 scans in the wave number range of 4000-550 cm^{-1}.

^{1}H and ^{13}C nuclear magnetic spectroscopy (^{1}H and ^{13}C NMR)

The ^{1}H-NMR and ^{13}C-NMR spectra were obtained on a BRUKER, Avance DPX model spectrometer, operated at a frequency of 300 MHz for ^{1}H and of 75 MHz for ^{13}C. Deuterated chloroform ($CDCl_3$) was used to dissolve the samples, and tetramethylsilane (TMS) was used as an internal standard.

Differential Scanning Calorimetry (DSC)

The DSC analyses were made using a Mettler-Toledo DSC 823e, using 5 mg samples in aluminum pans. Non-isothermal measurements were made with a heating rate of 10°C min^{-1}, in a temperature range of 30 to 400 °C, under nitrogen (N_2) purge at a flow rate of 50 mL min^{-1}.

Thermogravimetric Analyses (TGA)

The TGA analyses were carried out using a Mettler-Toledo TGA/SDTA851e using 5 mg samples placed in an alumina pan. The measurements were performed from 30°C to 800°C, at a scanning rate of 10°C min^{-1} under nitrogen (N_2) atmosphere at a flow rate of 50 mL min^{-1}.

Dynamic Mechanical Analyses (DMA)

DMA were conducted on a Mettler-Toledo DMA-1, using a single cantilever mode, at a heating rate of 3°C min^{-1} from 30 to 250 ºC, and a frequency of 1 Hz under air. The deformation applied was within the linear viscoelastic limit, determined by a sweep strain test.

Mechanical Analysis

A three-point bending test was performed using a universal testing machine Instron (Instron, model 3345, Canton, USA). The crosshead speed was set at 0.5 mm/min and one sample of each polybenzoxazine, with 80 mm X 4.3 mm X 1.3 mm dimension, was used with a useful length of 70 mm.

Method for microwave-assisted synthesis of CNSL-fu

In a 125 mL round-bottom flask equipped with a stirring bar was added CNSL (20.00 g), paraformaldehyde (5.60 g, 184.8 mmol) and furfurylamine (7.25 g, 73.9 mmol). The flask was placed in the microwave and fitted with a 50 cm Vigreux column and distillation head. The microwave was programmed to increase from room temperature to 100°C for 5 min, using maximum power of 500 W. After the stabilization of the temperature, the reaction continued for more 5 min. At the end of the reaction, the material was cooled to room temperature. The reaction mixture was diluted with ethyl acetate (250 mL) and this organic solution was washed in a separating funnel with an aqueous solution of 2 mol L^{-1} NaOH (3 X 150 mL) and with distilled water (3 X 150 mL). Finally, the organic phase was collected, dried over sodium sulphate, filtered, concentrated under reduced pressure and a dark brown viscous liquid was obtained 24.84 g. The chemical structures were characterized by ^{1}H-NMR, ^{13}C-NMR and FTIR and compared with the previous published results (A. ATTANASI et al., 2012) indicating the success of the procedure.

^{1}H RMN ($CDCl_3$, 300MHz, δ) 7.42 (s,1H), 6.84 (d, 7.6 Hz,1H), 6.73 (d, 7.7 Hz, 1H), 6.65 (s, 1H), 6.34 (m, 2H), 5.36 (m, 3H), 5.00 (m, 1H), 4.87 (m, 2H), 3.99 (s, 2H), 3.93 (m, 3H), 2.80 (m, 2H), 2.54 (t, 7.6 Hz, 2H), 2.05 (m, 4H), 1.60 (m, 2H), 1.32 (m, 15H), 0.89 (m, 2H). **^{13}C RMN** ($CDCl_3$, 75MHz, δ): 153.9, 153.5, 151.9, 144.4, 143.1, 142.7, 141.6, 137.0, 132.1, 130.6, 130.1, 130.0, 129.5, 128.5, 128.4, 128.2, 128.0, 127.8, 127.6, 127.0, 121.7, 121.2, 117.3, 116.9, 116.4, 115.2, 114.9, 110.5, 110.4, 109.1, 107.3, 82.0, 56.5, 49.6, 48.4, 39.1, 35.9, 32.0, 31.7, 31.5, 30.0, 29.9, 29.8, 29.6, 29.5, 29.4, 29.2, 27.4, 27.4, 25.9, 25.8, 23.0, 22.8, 14.3, 14.0. **FTIR** (ATR-ZnSe, cm^{-1}): 1578 (stretching of furan ring), 1504 (stretching of trisubstituted benzene ring), 1240 (C-O-C asymmetric stretching), 915 (benzoxazine related mode).

Method for microwave-assisted synthesis of ***CT-fu*** *(3,8-bis(furan-2-ylmethyl)-2,3,4,7,8,9-hexahydrobenzo[1,2-e:4,3-e']bis([1,3]oxazine)*

CT-fu was synthesized using a modified method as published previously by our group (KOTZEBUE et al., 2018). In a 250 mL round-bottom flask equipped with a stirring bar was added PEG (50 mL) and then heated till 80 ºC. Catechol (10.00 g, 89.91 mmol), paraformaldehyde (13.62 g, 449.55 mmol) and furfurylamine (17.64 g, 179.82 mmol) were added into the hot PEG and then stirred for 3 min to form a light red suspension. The flask containing the mixture was placed in the microwave and fitted with a 50 cm Vigreux column and distillation head. The Microwave was set to a maximum power of 500 W, temperature was programmed to increase from 60 to 120 °C in a period of 2 min; and kept at this temperature for additional 5 min, totaling 7 min under microwave irradiation. After the completion of the reaction, the mixture was put to cooled till room temperature forming a bulky solid phase. The reaction mixture was washed with 100 mL of methanol and transferred to an Erlenmeyer (250 mL). The mixture was sonicated in an ultrasound bath (40 kHz) at 40 ºC for 2 h and then a vacuum filtration was performed. The residue was washed once more and then put to dry in an oven at 80 ºC to overnight for solvent evaporation, obtaining a 23.15 g (72 % yield) white powder. The chemical structures were characterized by ^{1}H NMR, ^{13}C NMR and FTIR.

^{1}H RMN ($CDCl_3$, 300MHz, δ) 7.42 (d, 2 Hz, 1H), 6.51 (s, 1H), 6.34 (m, 1H), 6.27 (m, 1H), 4.99 (s, 2H), 4.00 (s, 2H), 3.970 (s, 2H,); **^{13}C RMN** ($CDCl_3$, 75MHz, δ): 151.8, 142.7, 119.0, 118.7, 110.4, 109.1, 82.7, 49.3, 48.6; **FTIR** (ATR-ZnSe, cm^{-1}): 1577 (stretching of furan ring), 1478 (stretching of tetrasubstituted benzene ring), 1235 (C-O-C asymmetric stretching), 923 (benzoxazine related mode)

(Co)polymerization of the bio-based benzoxazines

CNLS-fu and the combined mixtures with **CT-fu**, as described in Table 5, were put in silicone molds (40 X 20 X 2 mm) and melted at 140 °C in a vacuum oven. The polybenzoxazines were obtained using the following heating ramp: 140 ºC for 1 h, 160 ºC for 1 h, 180 ºC for 1 h and 200 ºC for 2h. A post-cure treatment was performed at 220 ºC for 2 h and 240 ºC for 2h. The sample mass used in the polymerization was approximately 1.5 g.

Table 5 - Composition of bio-based bis-benzoxazine resins

Sample	**CT-fu (%)**	**CNSL-fu (%)**
CNSL/CT10	10	90
CNSL/CT20	20	80
CNSL/CT 30	30	70
CNSL/CT 40	40	60
CNSL/CT 50	50	50

Source: The author

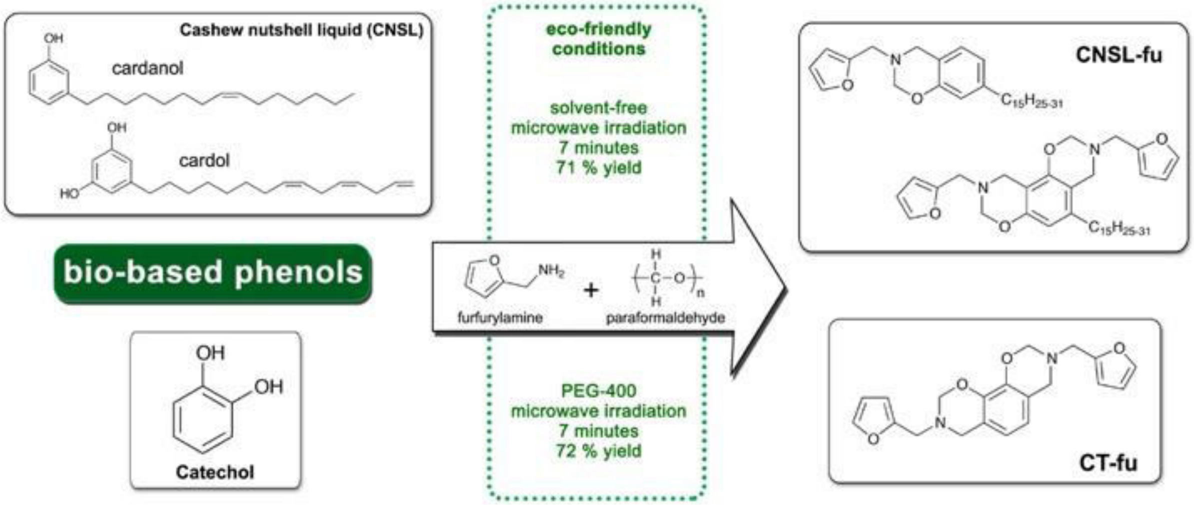
Results and discussion

Microwave-assisted synthesis of CNSL-fu and CT-fu

Bearing in mind the wide application of the benzoxazines resins in the industrial and academic sectors for polymeric materials, which usually require large quantities of starting material for its production and considering this with environmental concerns, the use of widely available eco-friendly resources has induced great interest (HÜLSEY; YANG; YAN, 2018; ISIKGOR; BECER, 2015; SHELDON, 2018b; VOIRIN et al., 2014). In this sense, CNSL and catechol were chosen as starting materials for the development of polybenzoxazines in this work.

The benzoxazines monomers derived of CNSL and catechol synthesized with the furfurylamine were obtained by means of a one-step reaction and under microwave irradiation (Scheme 5).

Scheme 5 - Synthesis of benzoxazine monomers CNSL-fu and CT-fu



Source: The author

Microwave-assisted synthesis of bio-based benzoxazines has been reported in the literature as highly efficient procedure. This synthesis has low reaction times and similar or higher yields when compared to traditional heating (KOTZEBUE et al., 2018; OLIVEIRA et al., 2017).

The efficiency of the microwave-assisted synthesis can be attributed to the interaction between organic molecules with the electric component of the microwave irradiation. The phenomenon of warming promoted by irradiation for microwaves resides in the dielectric heating, which is the ability of some compounds to transform electromagnetic energy into heat (RODRÍGUEZ et al., 2015). This ability is closely related to the polarity of these compounds.

CNSL is mainly composed by cardanol (81%), cardol (15%) and minor quantities of 2-methyl cardol, compounds that present an aliphatic side-chain containing up to 3 unsaturations (LOMONACO; MELE; MAZZETTO, 2017). For the **CNSL** employed in this work, the majority of cardanol was found as monounsaturated (80%) compound, while cardol as triunsaturated (63%)

one. Therefore, **CNSL-fu** was composed by both mono- and bis-benzoxazines, as depicted in Scheme 5.

The bio-based benzoxazine resin **CNSL-fu** was obtained from **CNSL**, furfurylamine and paraformaldehyde in conditions complete absence of solvents, since, except for paraformaldehyde, the reagents are liquids at room temperature, providing the complete solubilization of the reaction medium. The fast synthesis of **CNSL-fu** under microwave irradiation in just 7 minutes proved to be very promising, once it is reported in the literature that the synthesis of benzoxazines monomers from cardanol are usually obtained with reaction times lasting hours or days (A. ATTANASI et al., 2012; AMBROŽIČ; ŠEBENIK; KRAJNC, 2015; RIBEIRO et al., 2017).

Catechol-based benzoxazine (**CT-fu**) was obtained as related in the literature (KOTZEBUE et al., 2018), starting from catechol, furfurylamine and paraformaldehyde, and with the use of PEG as a nontoxic solvent. The synthesis of catechol-based benzoxazine under microwaves irradiation proved again to be very promising, due to short reaction time (7 min), compared with other bis-benzoxazine syntheses using traditional heating methods and toxic solvents, with reaction times of around 24 h (LIU; CHOU, 2005).

It is worth emphasizing the importance of obtaining benzoxazines resins in large quantities, once it is used in the field of polymer and materials science. The use of sources with a high amount of feedstock to obtain new bio-based benzoxazines, and a versatile methodology that requires a few minutes of reaction and generates good amounts of material, is a promising study with great potential to be exploited in a vast area of the science of polymers and materials.

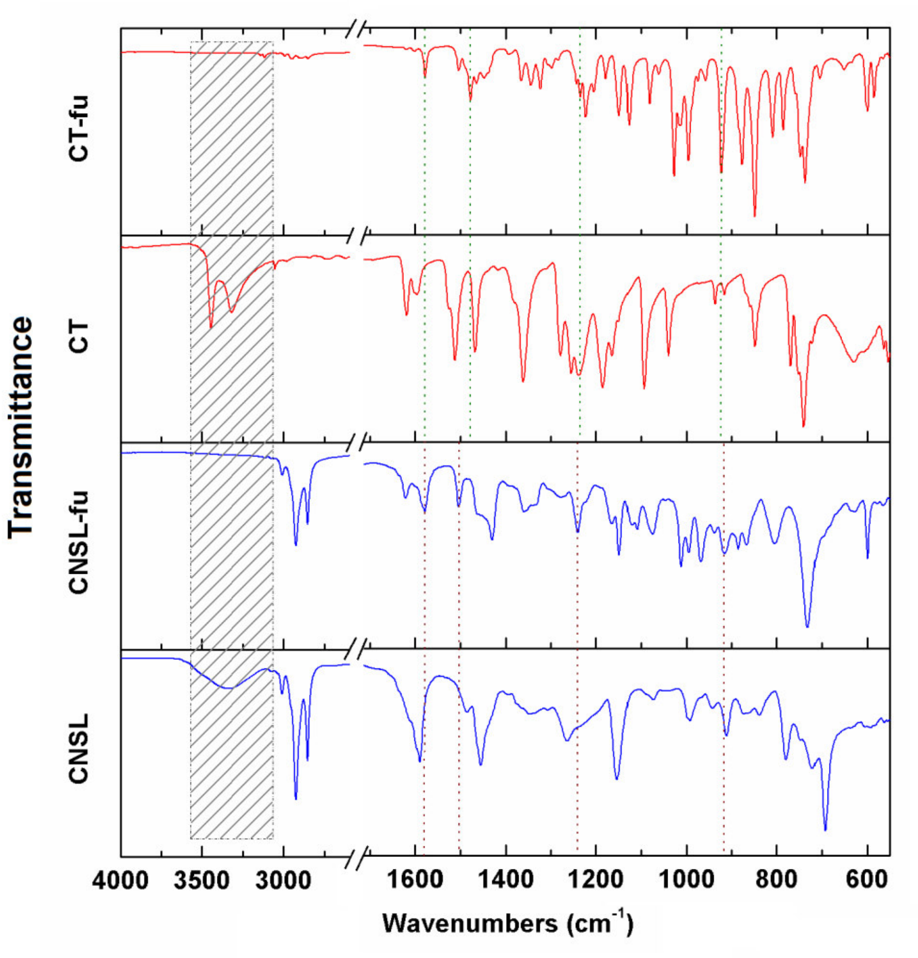
Structural characterization of bio-based benzoxazines

In order to determine the purity and the chemical structure of benzoxazines synthesized from CNSL and catechol, the obtained products were investigated by FTIR and ^{1}H NMR.

Figure 27 shows the FTIR spectra of the CNSL and its respective benzoxazine. In the spectrum of the benzoxazine monomer (**CNSL-fu**), the absence of the band at 3351 cm $^{-1}$, assigned to the O-H bond stretching, indicated the transformation of the hydroxyl group. The band at 1578 cm $^{-1}$ was attributed to the vibrational mode of the furan ring (LIU; CHOU, 2005). The absorption band at 1504 cm $^{-1}$ was referred to the C=C stretching of the trisubstituted benzene ring of the **CNSL-fu**. In addition, the formation of the fused oxazine ring on the benzene ring was confirmed by the appearance of the absorption bands at 1239 cm $^{-1}$, referred to the =C-O-C group and by the band at 915 cm^{-1} , a vibrational mode characteristic to benzoxazines (LIU; CHOU, 2005).

The structure of the benzoxazine monomer **CT-fu** was also confirmed by FTIR (Figure 27). The absence of the broad band at 3441 cm^{-1}, attributed to the of the O-H bond stretching, indicates the transformation of the hydroxyl group. The 1579 cm $^{-1}$ band is attributed to the vibrational mode of the furan ring (LIU; CHOU, 2005), and the presence of the oxazine ring is indicated by the bands 1478, 1235 and 923 cm^{-1} assigned to the C=C stretch of the tetra-substituted benzene ring, to asymmetric stretching =C-O-C and to benzoxazine related mode, respectively.

Figure 27 - FTIR spectra of CNSL, catechol (CT) and their benzoxazine derivatives (CNSL-fu and CT-fu).



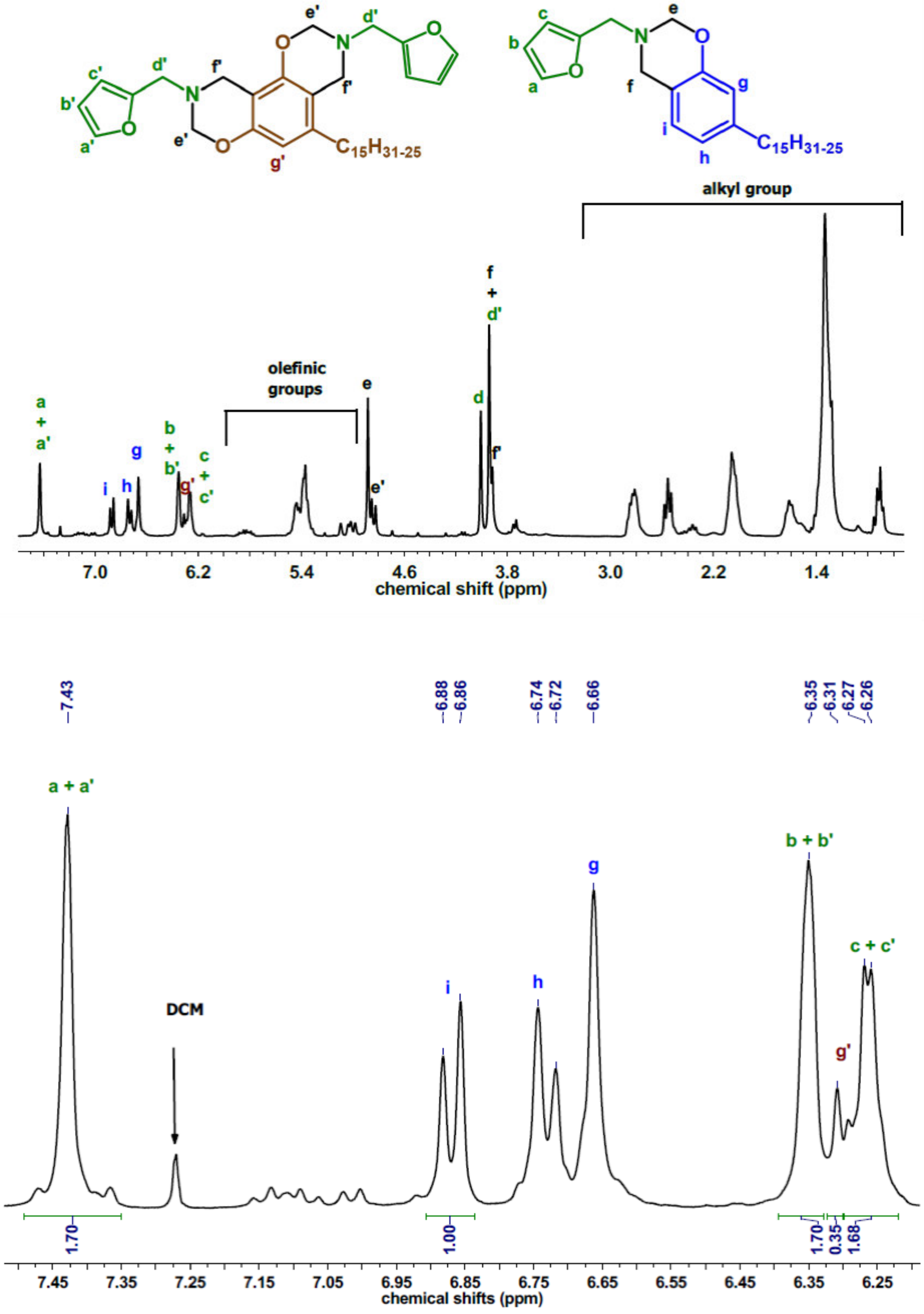
Source: The author

More detailed structural information was obtained of the synthesized monomers, **CNSL-fu** and **CT-fu**, through ^{1}H NMR analyses.

For the benzoxazine characterization by ^{1}H NMR, the identification of the methylene hydrogens of the oxazine rings are of most importance. The peaks observed at 4.79 to 4.93 ppm and at 3.90 to 3.96 ppm are attributed to the O-**CH_2**-N and the Ar-**CH_2**-N hydrogens, respectively, which indicated the formation of the oxazine rings. The aliphatic chains of the benzoxazines were observed by the peaks at the range of 0.80 to 2.90 ppm, representing the alkyl groups, and by the peaks at the range of 4.95 to 5.95 ppm, representing the olefinic groups. The peaks observed at 6.20 to 7.50 ppm are referred to the aromatic hydrogens (Figure 28).

Analyzing the aromatic region (Figure 28), it was possible to perform a semi-quantitive analysis of the composition of cardanol- and cardol-based benzoxazines in **CNSL-fu**. Specific individual peaks related to each of the two monomers were identified by the doublet at 6.87 ppm, referred to the hydrogen **i** of the cardanol-based benzoxazine, and the singlet at 6.31 ppm, referred to the solely benzene hydrogen **g’** of the cardol-based bis-benzoxazine (A. ATTANASI et al., 2012). After comparing the integrals of the peaks related to hydrogen **i** with hydrogen **g’** of 1.00 and 0.35, respectively, it was estimated that **CNSL-fu** was composed of around 26 % (mol/mol) of cardol-based benzoxazine. This estimated composition of the bis-benzoxazine was also confirmed by analyzing the integrals of the peak of hydrogen **i** with the peaks referred to the α- and β-hydrogens of the furan groups (**a**, **a’, b, b’, c** and **c’)** of the two monomers.

Figure 28 - ^{1}H NMR spectra of CNSL-fu



Source: The author

Sustainable Metrics of Benzoxazine Syntheses

Looking forward to evaluating the "greenness" of these two benzoxazine monomers, we also investigated their synthetic processes based on the two most known sustainable metrics: Atom Economy (AE) and Environmental Factor (E factor) (SHELDON, 2018a). The detailed calculations of these sustainable metrics are available as Supporting Information while the obtained values are summarized in Table 6.

To the best of our knowledge, this is the first time where sustainability indicators are applied for the syntheses of benzoxazine resins.

Table 6 - Sustainable Metrics of the syntheses of benzoxazine resins.

Benzoxazine	AE (%)	E-factor
CNSL-fu	~ 90	11.23
CT-fu	83	10.05

Source: The author

Atom Economy (AE)

Being part as one of the twelve principles of *Green Chemistry*, Atom Economy is the simplest and most known sustainable metric (ANASTAS; WARNER, 1998). According to Trost, AE can be understood as how much of the reactants is part of the product (TROST, 1991), in other words, it is the ratio of the molar weight of the product by the sum of the molar weights of the reactants. The ideal AE value is 100 %, meaning that all the reactants used ended up in the product. Using this concept for the benzoxazine syntheses of this work, it was observed that their AE values were at least 83 %. Because of the loss of at least two water molecules, it can be concluded that benzoxazine reactions can be overall quite sustainable. And the higher the molecular weights of the chosen phenolic compound and/or primary amine, the higher the AE values, as it was observed for the synthesis of **CNSL-fu**.

Environmental Factor (E factor)

Atom Economy has one main disadvantage, which is, it cannot determine the amount of waste produced during a reaction. Therefore, another sustainable index was used in order to overcome this drawback and provide more consistent information about benzoxazine synthesis sustainability.

Prof. Roger Sheldon came up with an interesting metric called Environmental Factor, or also known as the "E factor", which is a useful way to quantify the waste production of a chemical process (SHELDON, 1992, 2018a). The E factor is calculated by taking into account the mass of all materials used in the whole process, minus the mass of the desired product, divided by the mass of the desired product. An exception that has been taken is water, since counting this would lead to very high and unreasonable E factor results (SHELDON, 2018a). The lower this factor, the more sustainable the process is considered. The ideal E factor value would be zero.

This sustainable metric was used for the two benzoxazine syntheses of **CNSL-fu** and **CT-fu**, demonstrating that their E factors were around 11, classifying them in the industry segment of fine chemicals (SHELDON, 2018a). Unfortunately, the E factors of the two benzoxazine syntheses methods may not be compared between them, as the processes used and the obtained products are not the same. However, the production of benzoxazine resins can be highly sustainable for thermoset applications, where further purifications of these resins are not necessarily required. Using as an example the benzoxazine synthesis method of **H-Fa** and **R-Fa** of Dumas and coworkers (DUMAS et al., 2016b), no work up were performed after the completion of the reactions, demonstrating that benzoxazine synthesis can reach very low E factors.

Using Atom Economy and Environmental factor for the benzoxazine syntheses of **CNSL-fu** and **CT-fu** demonstrated to be important to have an idea how sustainable these methods are. And it was also understandable which variables can be altered when seeking for a more sustainable pathway to synthesize the resin of choice.

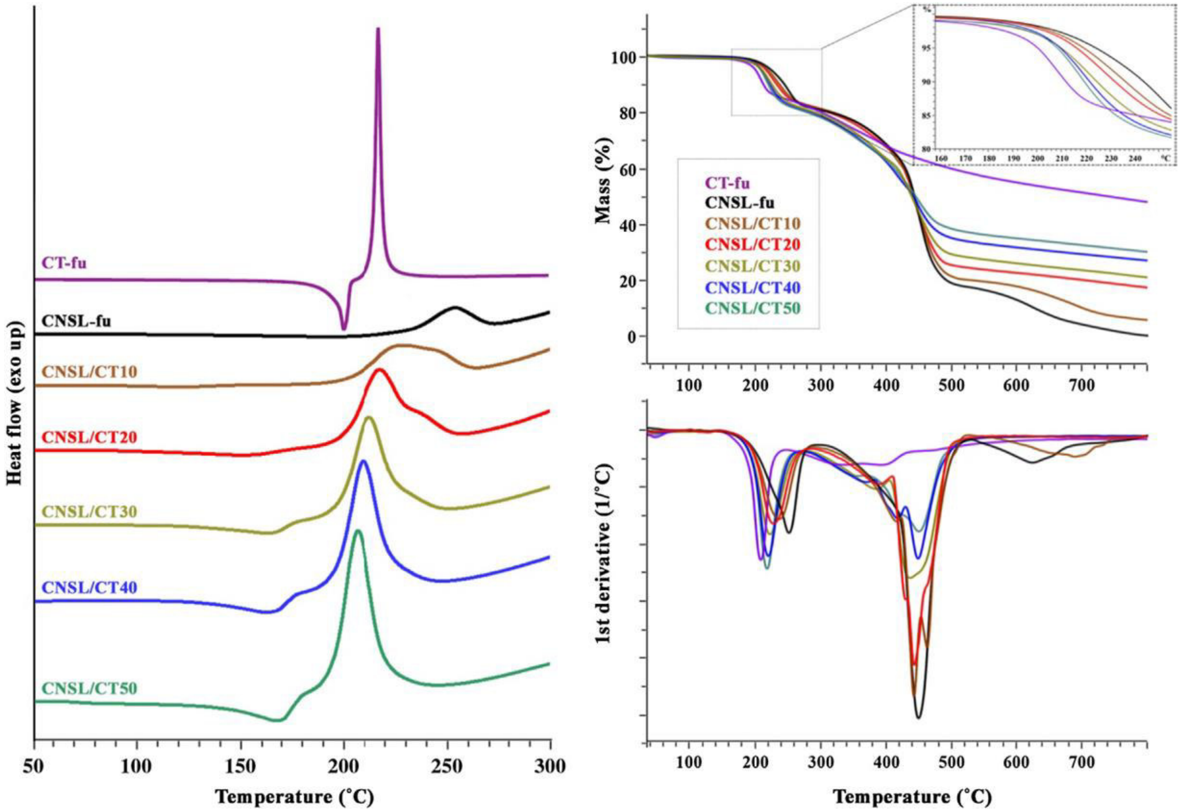
Nevertheless, some parameters of the benzoxazine syntheses of **CNSL-fu** and **CT-fu** were not considered in these metrics but are worth to be mentioned, since they indicate that these resins and methods can be even more sustainable than as demonstrated by the metrics, which are:

1. CNSL and lignocellulosic feedstocks as starting materials (low-cost, widely available, no food-chain hampering issues);
2. Methods employed solvent-free system or atoxic PEG as solvent;
3. Microwave-assisted heating (effective and fast heating, meaning higher energy saving);
4. Recyclability of solvents used (ethyl acetate and methanol).

Polymerization behavior of bio-based copolymers

Non-isothermal differential scanning calorimetry (DSC) analyses were performed of **CNSL-fu** and its mixtures with **CT-fu**, prepared in various molar ratios, to provide a better understanding of the polymerization behavior of each sample (Figure 29). **CT-fu** monomer was not analyzed for this work, as it has already been reported previously (KOTZEBUE et al., 2018). The initial (T_e) and maximum (T_p) polymerization temperatures as well as the melting points (T_m) of bio-based benzoxazines and mixtures are summarized in Table 7.

Figure 29. DSC and TGA curves of CNSL-fu and CT-fu monomers and mixtures



Source: The author

Table 7. DSC data from CNSL-fu and its mixtures with CT-fu

Monomers	***DSC***					***TGA***		
	T_m (°C)	***T_e (°C)***	***T_p (°C)***	***Oxazine ring (mmol/g)***	***ΔH_p (J/g)***	***T_e (ºC)***	***T_5 (ºC)***	***Char Yield (%)***
CNSL-fu	-	233	253	2.66	16.8	209	221	0
CNSL/CT10	-	205	225	2.95	49.0	206	218	5.4
CNSL/CT20	-	201	217	3.25	77.2	203	215	17.0
CNSL/CT30	165	199	212	3.56	95.5	201	209	20.7
CNSL/CT40	164	197	209	3.87	118.8	201	208	27.7
CNSL/CT50	168	195	206	4.17	136.4	201	207	29.8
CT-fu[22]	198	213	220	5.7	381.0	192	199	47.6

Source: The author

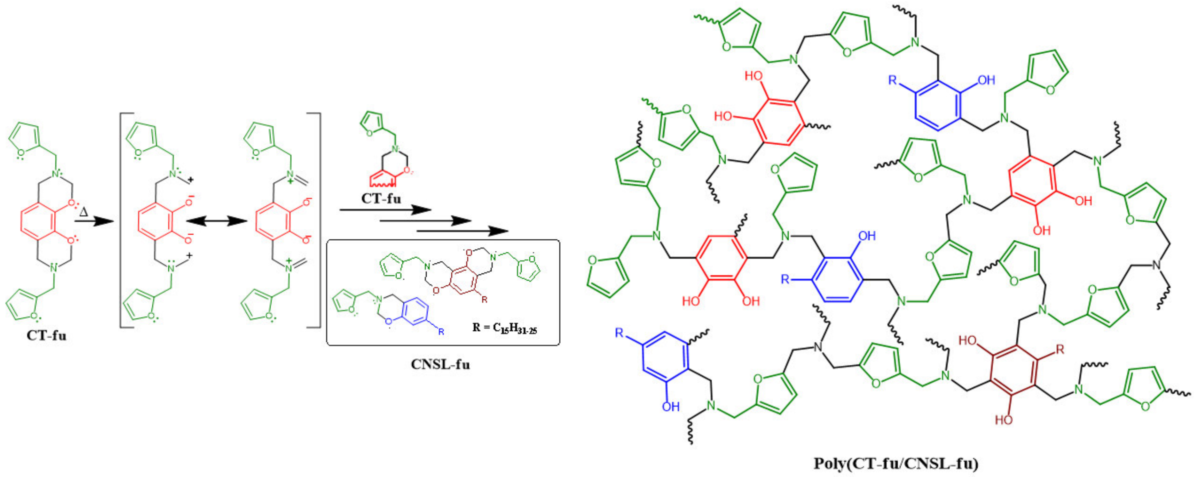
In the DSC thermograms of **CNSL-fu** it was observed two exothermic events as expected for typical cardanol-based benzoxazines. The first exothermic event, between 220 to 280 °C, is regarded to the ring-opening polymerization of the oxazine ring and the second event, between 280 to 400 °C, is referred to the polymerization of the olefinic groups of the aliphatic chains. The T_p of **CNSL-fu** was 10 °C lower than the **Ca-FA-BOX** of Ambrožič and co-workers (AMBROŽIČ; ŠEBENIK; KRAJNC, 2015), which used pure cardanol and furfurylamine as starting materials. Despite that **CNSL-fu** is mainly constituted of cardanol-based benzoxazines, the presence of cardol-based benzoxazines, which are bis-benzoxazines, may be promoting the polymerization to occur at lower temperatures.

Considering that CNSL-based benzoxazines demonstrate low mechanical properties and **CT-fu** is extremely difficult to be homopolymerized due to its narrow processing window, as reported in the previous work (KOTZEBUE et al., 2018), it was proposed to mix the liquid **CNSL-fu** and the solid **CT-fu** in different ratios, looking forward obtaining a better high-performance CNSL-based polybenzoxazine. The relation of the ratios of the mixed resins and the thermal and thermomechanical properties of their respective copolymers was investigated.

Analyzing the polymerization behavior of the mixtures, no endothermic events were observed on **CNSL/CT10** and **CNSL/CT20**, demonstrating that **CT-fu** was well dissolved in **CNSL-fu**, and the good compatibility of the monomers. On the other hand, the DSC curves of the other systems (**CNSL/CT30**, **CNSL/CT40** and **CNSL/CT50**) presented small endothermic events at around 150 to 180 °C, indicating the presence of insoluble **CT-fu** in the mixtures. Nevertheless, as the melting enthalpy of these mixtures are very low, indicating small amounts of insoluble **CT-fu**, it is possible that these resins will provide imperfect-free copolymers after curing.

After analyzing the exothermic events of the mixtures, it was observed that by increasing their **CT-fu** content, the initial polymerization temperature (T_e) and maximum (T_p) temperature of the mixtures decreased gradually, demonstrating that the ROP process is initiated predominantly by **CT-fu** reacting further with the other monomers (Scheme 6). This behavior was also observed in a previous work (KOTZEBUE et al., 2018).

Scheme 6 - Proposed copolymerization of CT-fu and CNSL-fu



Source: The author

Another interesting observation was the increase of the polymerization enthalpy (*ΔH*) of the systems with the increasing content of **CT-fu**. This results can be correlated to the oxazine-ring concentration of each system (Table 7), since **CT-fu** has an elevated concentration of oxazine rings (mmols/gram) of monomers.

A previous work correlated the increase/decrease of the enthalpy of copolymerization of benzoxazine monomers with the formation of volatiles during the polymerization process (DUMAS et al., 2015b). In our work it is not the same case, since **CNSL-fu**, which has a lower *ΔH*, presented a higher boiling point than **CT-fu**, as observed by TGA analysis (Figure 29 and Table 7).

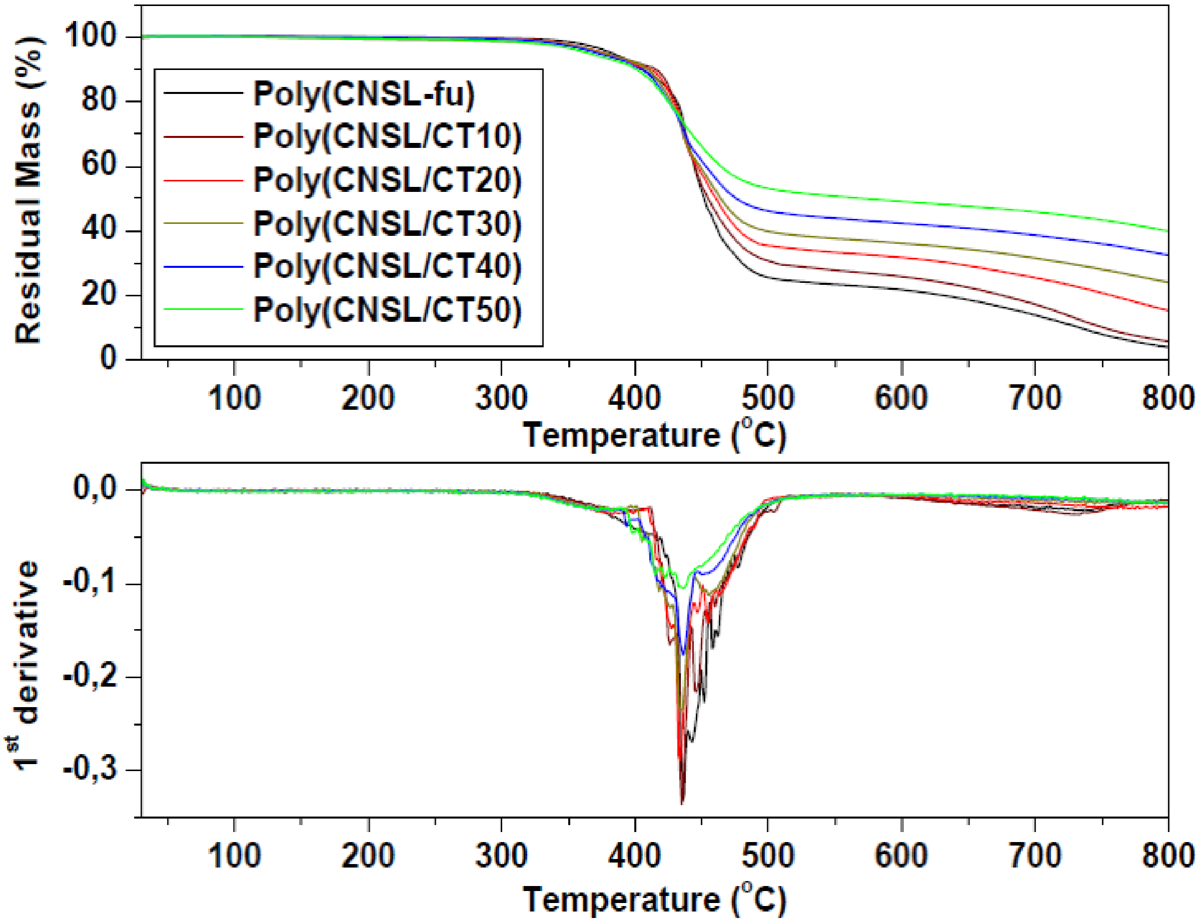
After the thermal characterizations of the monomers and the mixtures, they, except for **CT-fu**, where (co)polymerized and then put to be post-cured as described in the Experimental section.

Evaluation of the thermal and mechanical properties of (co)polybenzoxazines

Thermogravimetric analysis (TGA)

The thermal stability of the **CT-fu/CNSL-fu** polybenzoxazines was studied by thermogravimetric analysis (TGA) under inert atmosphere (N_2) and their TGA curves are shown on Figure 30. The obtained results of the polybenzoxazines are expressed in Table 8.

Figure 30 - TGA thermograms of (co)polybenzoxazines



Source: The author

Table 8 - Thermal Properties of (co)polybenzoxazines obtained by TGA

Compound	***T_5 (°C)***	***T_{max} (°C)***	***Char Yield (%)***	***LOI***
Poly(CNSL-fu)	381	441	4	19.1
Poly(CNSL/CT10)	376	438	6	19.9
Poly(CNSL/CT20)	374	433	15	23.5
Poly(CNSL/CT30)	374	433	24	27.1
Poly(CNSL/CT40)	370	434	32	30.3
Poly(CNSL/CT50)	364	435	40	33.5

Source: The author

In the literature is described that cardanol-based benzoxazines have superior thermal stability when compared with BPA-based benzoxazines (LOCHAB; VARMA; BIJWE, 2010). This observation was also confirmed in this work.

It was observed that **Poly(CNSL-fu)** had an impressive high thermal stability as it can be observed by its 5% weight loss temperature (T_5) of 381 °C, which was not expected as its polymer structure possesses a large number of aliphatic groups. By analyzing the influence of **CT-fu** in the copolymers (Table 8), it was observed that as the **CT-fu** content increased, the lower the T_5 of the polymers. Even though that **Poly(CNSL/CT50)** had de lowest T_5 among the polybenzoxazines, the 50% (w/w) increment reduced its 5% weight loss temperature only with 17 °C when compared with **Poly(CNSL-fu)**.

These fully bio-based polybenzoxazines possess good thermal stabilities in the initial phase of degradation when compared with BPA-based polybenzoxazines. For example, furan-BPA-based polybenzoxazines **P-BPA-FBz** (LIU; CHOU, 2005) and **Poly(BA-fu)** (KOTZEBUE et al., 2018) had a T_5 of 347 and 361 °C, respectively. And aniline-BPA-based polybenzoxazine of the commercially available **XU 35610** had a T_5 of 313 °C (HUNTSMAN, 2018).

The insertion of the **CT-fu** monomer demonstrated that all the copolymers had an increase in the carbonization yield when compared to **Poly(CNSL-fu)**. For example, the **Poly(CNSL/CT50)** had a 36 % increase in char yield when compared with **Poly(CNSL-fu)**. The **Poly(CNSL/CT40)** and **Poly(CNSL/CT50)** had higher char yields (at 800 °C) than of **Poly(BA-a)**, which ranges from 28.5 to 30.0 % (DAYO et al., 2017; ISHIDA; SANDERS, 2000;

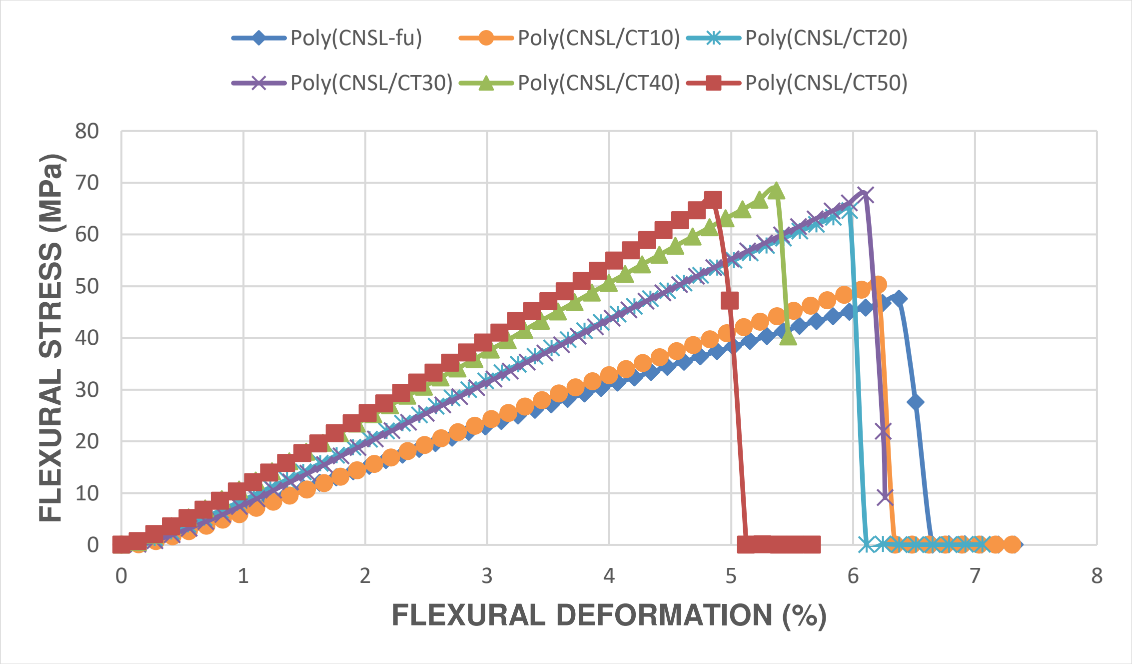
KOPSIDAS; HAMERTON, 2016). The fact that **Poly(CNSL/CT40)** and **Poly(CNSL/CT50)** possess high char yields could indicate that these copolymers have high flame retardancy properties.

And indeed, by using the van Krevelen equation (VAN KREVELEN, 1975) it was noticed that **Poly(CNSL/CT40)** and **Poly(CNSL/CT50)** possess estimated LOI values of 30.3 and 33.5, respectively. Knowing that materials with LOI values of > 28 are considered self-extinguishing (MALLAKPOUR; ZADEHNAZARI, 2017), these two copolymers can be considered as a BPA-, halogen-, phosphor-, and silane-free fully bio-based flame retardants**.**

Mechanical Analysis

The mechanical properties of the polybenzoxazines were analyzed using a 3-point bending mode and their respective stress-strain curves are shown on Figure 31 and their data summarized on Table 9 and Figure 33.

Figure 31 - Stress-strain curves obtained from 3-point bending of polybenzoxazines



Source: The author

The stress-strain curves of the polybenzoxazines demonstrated only an elastic region, which is typical for brittle thermoset materials. Their high maximum flexural deformation (ε_f) could be attributed to the aliphatic chain which provides plasticity for the matrices. It was observed that with increment of **CT-fu** in the polymer matrices, the higher the flexural modulus (E_f) (Figure 31), which was expected as **CT-fu** is composed mainly of aromatic groups which increase the rigidity of the polymer matrices. With the 50 % increment of **CT-fu** in **poly(CNSL/CT50)**, the E_f of the polymer matrix was increased with 80 %, when compared with **poly(CNSL-fu)**.

Table 9 - Mechanical properties of polybenzoxazines obtained by 3-point bending mode

Compound	**E_f (GPa)**	**σ_f (MPa)**	**ε_f (%)**
Poly(CNSL-fu)	0.81	48	6.4
Poly(CNSL/CT10)	0.90	50	6.2
Poly(CNSL/CT20)	1.20	65	6.0
Poly(CNSL/CT30)	1.22	68	6.1
Poly(CNSL/CT40)	1.34	69	5.4
Poly(CNSL/CT50)	1.47	67	4.9

Source: The author

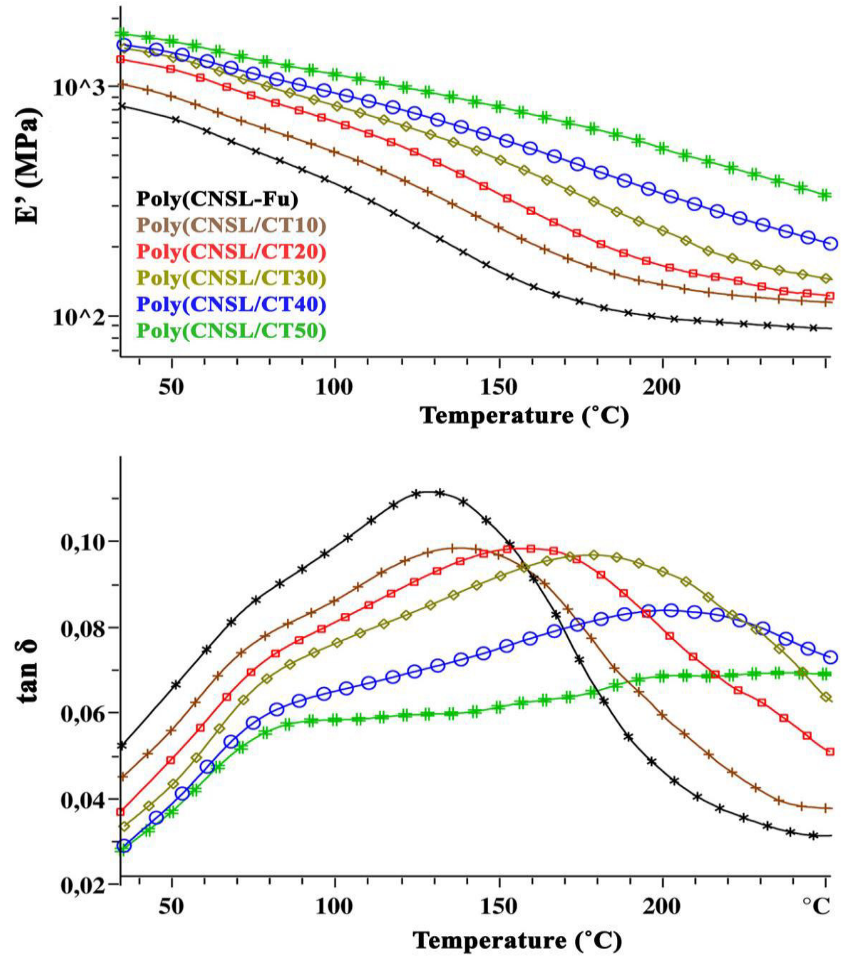
Dynamic Mechanical Analysis (DMA)

The thermo-mechanical properties of the polymers were analyzed by DMA (Figure 32) and their data are expressed on Table 10 and Figure 33 and 34.

It was observed that **Poly(CNSL-fu)** had a storage modulus (*E'*) at 30 ºC of 0.83 GPa, which is higher than the cardanol-based polybenzoxazine **pCDN-a** which had an *E'* of 0.54 GPa (RIBEIRO et al., 2017). This increase of the storage modulus is due to the presence of the cardol-based benzoxazines, which is a bis-benzoxazine, as determined by ^{1}H NMR (Figure 28) (A. ATTANASI et al., 2012).

The presence of **CT-fu** in the copolymers alter significantly the mechanical properties of the polybenzoxazines. The higher the **CT-fu** content of the copolymers, the higher their storage modulus. At 30 ºC (Figure 32 and 33), all the copolymers demonstrated to have a *E'* above 1 GPa. By replacing 50 % in weight the **CNSL-fu** with **CT-fu**, it was possible to double the storage modulus of the polymer, as **Poly(CNSL/CT50)** had an interesting *E'* of 1.70 GPa. This fully bio-based copolymer presents itself as a promising BPA-free high-performance material. Analyzing the storage modulus of **Poly(CNSL/CT50)** at higher temperatures, it was observed that at 100 ºC the *E'* of the polymer was still above 1 GPa, which is quite remarkable for cardanol-based polybenzoxazines.

Figure 32 -. DMA analyses of CT-fu/CNSL-fu copolymers



Source: The author

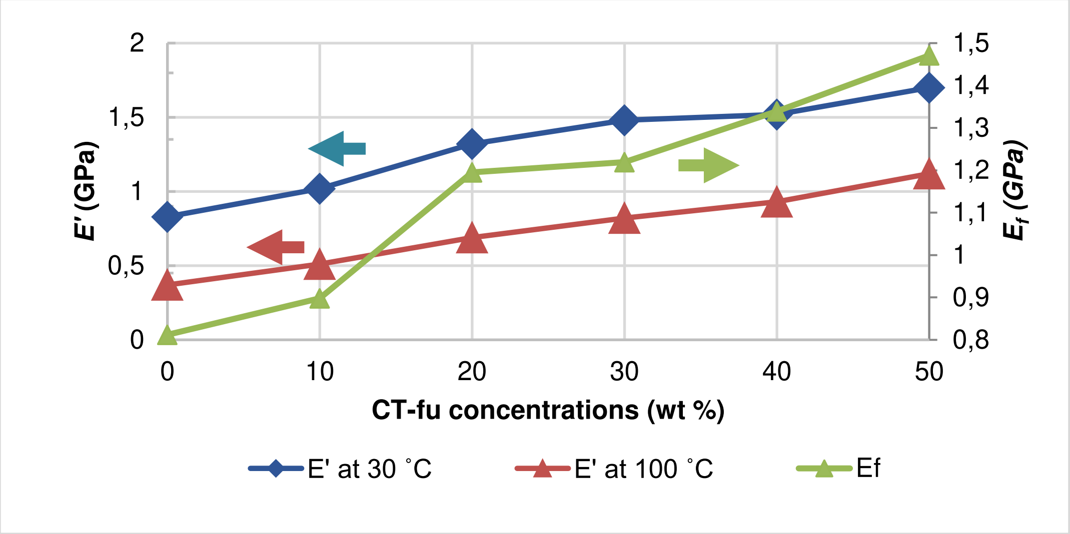
Table 10 - Thermo-mechanical properties of polybenzoxazines obtained by DMA Analyses

Polymer	***E'* at 30 ºC (GPa)**	***E'* at 100 ºC (GPa)**	***T_g* (ºC)**	***tan δ***	**ρx** (.10^{-3} mol/cm^3)
Poly(CNSL-fu)	0.83	0.37	129	0.110	4.98
Poly(CNSL/CT10)	1.02	0.51	138	0.099	5.34
Poly(CNSL/CT20)	1.32	0.69	156	0.098	5.48
Poly(CNSL/CT30)	1.48	0.82	178	0.096	5.72
Poly(CNSL/CT40)	1.52	0.93	202	0.084	N/D
Poly(CNSL/CT50)	1.70	1.12	> 250	< 0.07	N/D

Source: The author

The glass transition temperature (T_g) was determined by the peak maximum of the α-transitions (Figure 32). By correlating the **CT-fu/CNSL-fu** concentrations with the T_g of their respective polymers (Figure 32), it was observed that the higher the **CT-fu** insertion, higher the T_g of the polymers (Figure 33).

Figure 33 - Correlation of CT-fu/CNSL-fu concentration with *E'*

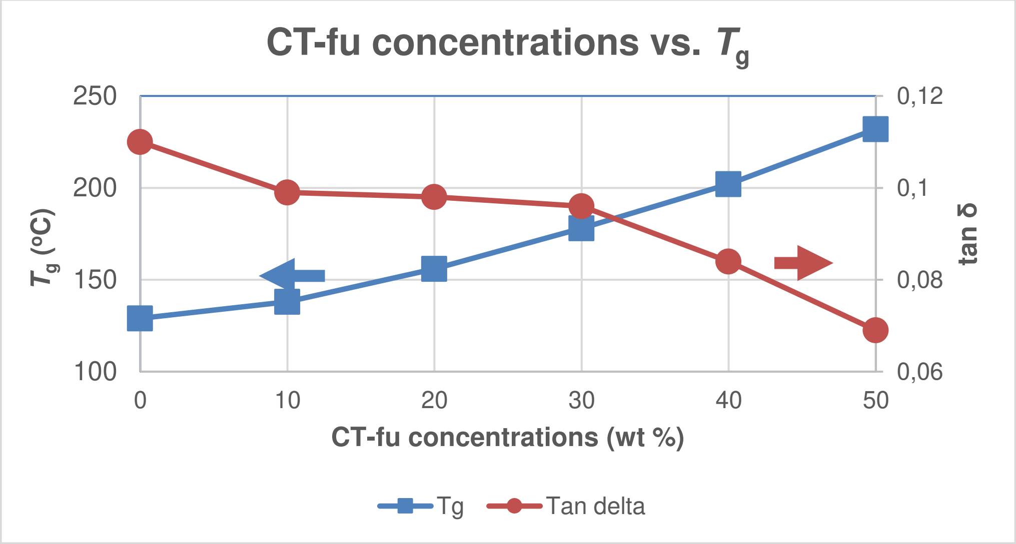


Source: The author

The glass transition temperature of **Poly(CNSL-fu)** was 129 ºC, which is higher than the other cardanol-based polybenzoxazines that range from 85 to 106 ºC (AMBROŽIČ; ŠEBENIK; KRAJNC, 2015; RIBEIRO et al., 2017). By adding **CT-fu** content in the polymer, it was demonstrated that **Poly(CNSL/CT20)** had a similar T_g of **Poly(BA-a),** which is 158 ºC (HUNTSMAN, 2018). With further addition of **CT-fu** in the polymer composition, it was possible to reach T_g above 200 ºC, as shown by **Poly(CNSL/CT40)**. The glass transition temperature of **Poly(CNSL/CT50)** could not be determined accurately, as no clear α-transition was observed. Even so, due to the linear increase tendency of **CT-fu** concentration from 10 to 40 % with the T_g of their respective polybenzoxazines, it can be estimated that **Poly(CNSL/CT50)** had glass transition temperature above 250 ºC.

Other relaxation activities were observed in the temperature range of 50 to 100 ºC (Figure 32), which is considered as β-transitions (NING; ISHIDA, 1994a), probably associated with pendant group movements (MENARD, 1999). These specific relaxations could be associated mainly by the mobility of aliphatic chains from cardanol and cardol.

Figure 34 - Correlation of CT-fu/CNSL-fu concentration with α transitions of the copolybenzoxazines



Source: The author

The stiffness, determined by the maximum *tan δ* value of the *α*-transition, of the polymers was also analyzed. The lower the *tan δ* value, higher the stiffness of the polymer. It was observed that the polymers had *tan δ* values varying between 0.08 and 0.11 (Figure 34). The higher the **CT-fu** content, higher the stiffness of the polymer, which is expected since this monomer is composed mainly of aromatic groups. As it was not possible to observe an *α*-transition of **Poly(CNSL/CT50)**, its maximum *tan δ* value was not defined. Even so, the fact that the *tan δ* value of this polymer did not reach a *tan δ* value higher than 0.08 indicate that **Poly(CNSL/CT50)** possesses a very high stiffness.

The cross-linking density (ρ_x) of the each polybenzoxazine was also determined by using the storage modulus at the rubbery plateau (E'_e) in the equation (Eq. 3) proposed by Nielsen (NIELSEN, 1969).

$$Log(E'_e/3) = 7 + 293\rho_x \qquad (Equation\ 3)$$

It was observed that as the **CT-fu** content increased in the polymer matrix, the higher cross-linking density, which was expected as bis-benzoxazine provides higher cross-linking than mono-benzoxazines. It was not possible to determine the cross-linking density of **poly(CNSL/CT40)** and **poly(CNSL/CT50)** as their respective storage modulus curves didn't reach the rubbery plateau till 250 °C.

Comparing the thermal properties of the polymers of the renewable resins of this work with the bisphenol A-based (**BA-a)** and other bio-based benzoxazine resins (Table 11), it was concluded that the fully bio-based **CNSL-fu/CT-fu** resins are very promising.

The polybenzoxazines containing 20 to 50% of **CT-fu** had similar or higher T_g and T_5 than of the commercial available **BA-a** and **poly(CNSL/CT40)** and **poly(CNSL/CT50)** had higher thermal stability than **poly(BA-a)** as it can be observed by their *CY'*s. This possibility to mix the **CNSL-fu** with **CT-fu** in different ratios can be seen as an advantage, since the thermal and mechanical properties of the polymers can easily be tuned for a desired application.

Other high-performance bi-functional bio-based benzoxazines, such as **C-pPDA**, **H-Fa** and **R-Fa**, demonstrated similar or higher thermal and thermo-mechanical properties than the **CNSL-fu/CT-fu** resins (Table 11). Unfortunately, the synthesis of these benzoxazines has one drawback. Their renewable starting materials, disregarding furfurylamine, are not commercially and widely available as CNSL and catechol.

Table 11 - Comparison of thermal properties of catechol- and CNSL-based polybenzoxazines with reported (bio-based) polybenzoxazines

Benzoxazine resin	**T_g (°C)**	**T_5 (°C)**	**CY at 800 °C (%)**
CNSL/CT20	156	374	15
CNSL/CT30	178	374	24
CNSL/CT40	202	370	32
CNSL/CT50	N/D	364	40
BA-a (KOPSIDAS; HAMERTON, 2016) (BPA and Aniline)	156-157	279	30
C-pPDA (DUMAS et al., 2016c) (Chavicol and 1,4-diaminobenzene)	~ 220*	-	-
	350**	413	~ 45
R-Fa (DUMAS et al., 2016b) (Resorcinol and furfurylamine)	270	335	~ 65
H-Fa (DUMAS et al., 2016b) (Hydroquinone and furfurylamine)	230	310	~ 65
U-da (XU et al., 2013) (Urushiol and DDM)	135	350	25

*cured at 250 °C; **cured at 300 °C

Source: The author

Conclusion

Cashew Nut Shell Liquid (**CNSL**) and lignocellulose are interesting renewable starting materials for large scale production of bio-based high-performance thermosetting resins as they are inexpensive and widely available. **CNSL**, catechol and furfurylamine were proven to be potential starting materials for the sustainable production of high-performance bio-based benzoxazine resins, **CNSL-fu** and **CT-fu**, since efficient eco-friendly methods were employed as determined by their sustainable metrics. As the liquid CNSL-based benzoxazine resins provide usually polybenzoxazines with low thermomechanical properties and the solid **CT-fu** possess poor processability issues, one resin can be used as a complement with the other, reaching copolymers with increased mechanical properties, highly stable thermal properties, glass transition temperatures above 200 ^{o}C and good flame retardancies. As the results demonstrate, these bio-based benzoxazine resins are interesting competitors against the BPA-based benzoxazine and other fossil-based thermosetting resins.

REFERENCES

A. ATTANASI, O. et al. Solvent Free Synthesis of Novel Mono- and Bis-Benzoxazines from Cashew Nut Shell Liquid Components. **Current Organic Chemistry**, v. 16, n. 21, p. 2613–2621, 1 nov. 2012.

AGAG, T.; JIN, L.; ISHIDA, H. A new synthetic approach for difficult benzoxazines: Preparation and polymerization of 4,4′-diaminodiphenyl sulfone-based benzoxazine monomer. **Polymer**, v. 50, n. 25, p. 5940–5944, nov. 2009.

AHMAD, F.; SILVA, E. L.; VARESCHE, M. B. A. Hydrothermal processing of biomass for anaerobic digestion – A review. **Renewable and Sustainable Energy Reviews**, v. 98, n. December 2017, p. 108–124, 2018.

ALTIN KARATAŞ, M.; GÖKKAYA, H. A review on machinability of carbon fiber reinforced polymer (CFRP) and glass fiber reinforced polymer (GFRP) composite materials. **Defence Technology**, v. 14, n. 4, p. 318–326, ago. 2018.

AMARNATH, N.; APPAVOO, D.; LOCHAB, B. Eco-Friendly Halogen-Free Flame Retardant Cardanol Polyphosphazene Polybenzoxazine Networks. **ACS Sustainable Chemistry & Engineering**, v. 6, n. 1, p. 389–402, 2 jan. 2018.

AMBROŽIČ, R.; ŠEBENIK, U.; KRAJNC, M. Synthesis, curing kinetics, thermal and mechanical behavior of novel cardanol-based benzoxazines. **Polymer**, v. 76, p. 203–212, out. 2015.

ANASTAS, P. T.; WARNER, J. C. **Green Chemistry: Theory and Practice**. New York: Oxford University Press, 1998.

BARANEK, A. D. et al. Flexible aliphatic-bridged bisphenol-based polybenzoxazines. **Polymer Chemistry**, v. 3, n. 10, p. 2892–2900, 2012.

BECKHAM, G. T. et al. Opportunities and challenges in biological lignin valorization. **Current Opinion in Biotechnology**, v. 42, n. March, p. 40–53, dez. 2016.

BERESKA, A. et al. The application of organophosphorus flame-retardants in epoxy resin. **Journal of Vinyl and Additive Technology**, v. 23, n. 2, p. 142–151, maio 2017.

BILAL, M. et al. Biotransformation of lignocellulosic materials into value-added products—A review. **International Journal of Biological Macromolecules**, v. 98, p. 447–458, 2017.

BOBADE, S. K. et al. Bio-Based Thermosetting Resins for Future Generation: A Review. **Polymer-Plastics Technology and Engineering**, v. 55, n. 17, p. 1863–1896, 2016.

BOMTEMPO, J.-V.; CHAVES ALVES, F.; DE ALMEIDA OROSKI, F. Developing new platform chemicals: what is required for a new bio-based molecule to become a platform chemical in the bioeconomy? **Faraday Discuss.**, v. 202, p. 213–225, 2017.

BRADY, J. et al. Developing Solid Oral Dosage Forms. In: QIU, Y. et al. (Eds.). . 2nd. ed. [s.l.] Academic Press, 2017. p. 1176.

BROWN, E. A.; RIDER, D. A. Pegylated Polybenzoxazine Networks with Increased Thermal Stability from Miscible Blends of Tosylated Poly(ethylene glycol) and a Benzoxazine Monomer. **Macromolecules**, v. 50, n. 17, p. 6468–6481, 2017.

BURKE, W. J. 3,4-Dihydro-1,3,2H-Benzoxazines. Reaction of p -Substituted Phenols with N,N-Dimethylolamines. **Journal of the American Chemical Society**, v. 71, n. 2, p. 609–612, fev. 1949.

BURKE, W. J. et al. A New Aminoalkylation Reaction. Condensation of Phenols with Dihydro-1,3-aroxazines. **The Journal of Organic Chemistry**, v. 30, n. 10, p. 3423–3427, 1965.

BURKE, W. J.; GLENNIE, E. L. M.; WEATHERBEE, C. Condensation of Halophenols with Formaldehyde and Primary Amines. **The Journal of Organic Chemistry**, v. 29, n. 4, p. 909–912, 1964.

BURKE, W. J.; MURDOCK, K. C.; EC, G. Condensation of Hydroxyaromatic Compounds with Formaldehyde and Primary Aromatic Amines. **Journal of the American Chemical Society**, v. 76, n. 6, p. 1677–1679, 1954.

BURKE, W. J.; SMITH, R. P.; WEATHERBEE, C. N,N-Bis-(hydroxybenzyl)-amines: Synthesis from Phenols, Formaldehyde and Primary Amines. **Journal of the American Chemical Society**, v. 74, n. 3, p. 602–605, 1952.

BURKE, W. J.; STEPHENS, C. W. Monomeric Products from the Condensation of Phenol with Formaldehyde and Primary Amines. **Journal of the American Chemical Society**, v. 74, n. 6, p. 1518–1520, mar. 1952.

BURKE, W. J.; WEATHERBEE, C. 3,4-Dihydro-1,3,2H-Benzoxazines. Reaction of Polyhydroxybenzenes with N-Methylolamines 1. **Journal of the American Chemical Society**, v. 72, n. 10, p. 4691–4694, out. 1950.

CALÒ, E. et al. Synthesis of a novel cardanol-based benzoxazine monomer and environmentally sustainable production of polymers and bio-composites. **Green Chemistry**, v. 9, n. 7, p. 754–759, 2007.

CHEN, J. et al. Polyethylene glycol and solutions of polyethylene glycol as green reaction media. **Green Chemistry**, v. 7, n. 2, p. 64–82, 2005.

CHEN, Z.; WAN, C. Biological valorization strategies for converting lignin into fuels and chemicals. **Renewable and Sustainable Energy Reviews**, v. 73, p. 610–621, jun. 2017.

CHIU, W.-M. et al. Preparation and characterization of novel polybenzoxazine hybrid materials. **High Performance Polymers**, v. 28, n. 8, p. 971–983, 2016.

CHOI, S.-W. et al. Synthesis, characterization and thermal degradation of functional benzoxazine monomers and polymers containing phenylphosphine oxide. **Polymer Degradation and Stability**, v. 91, n. 5, p. 1166–1178, maio 2006.

CINI, E.; PETRICCI, E.; TADDEI, M. Pd/C Catalysis under Microwave Dielectric Heating. **Catalysts**, v. 7, n. 12, p. 89, 20 mar. 2017.

DAI, J. et al. Biobased Benzoxazine Derived from Daidzein and Furfurylamine: Microwave-Assisted Synthesis and Thermal Properties Investigation. **ChemSusChem**, v. 11, n. 18, p. 3175–3183, 21 set. 2018.

DAYO, A. Q. et al. Natural hemp fiber reinforced polybenzoxazine composites: Curing behavior, mechanical and thermal properties. **Composites Science and Technology**, v. 144, p. 114–124, maio 2017.

DE LEON, A. C. et al. High performance polymer nanocomposites for additive manufacturing applications. **Reactive and Functional Polymers**, v. 103, p. 141–155, jun. 2016.

DENG, C. et al. Modes of action of a mono-component intumescent flame retardant MAPP in polyethylene-octene elastomer. **Polymer Degradation and Stability**, v. 138, p. 142–150, 2017.

DOUSE, E. et al. Modification of stress-strain behaviour in aromatic polybenzoxazines using core shell rubbers. **Reactive and Functional Polymers**, v. 103, p. 117–130, jun. 2016.

DRIOWYA, M. et al. **Microwave-assisted synthesis of bioactive six-membered heterocycles and their fused analogues**. [s.l: s.n.]. v. 21

DUMAS, L. et al. Eugenol-based benzoxazine: from straight synthesis to taming of the network properties. **J. Mater. Chem. A**, v. 3, n. 11, p. 6012–6018, 2015.

DUMAS, L. et al. Arbutin-based benzoxazine: en route to an intrinsic water soluble biobased resin. **Green Chem.**, v. 18, n. 18, p. 4954–4960, 2016a.

DUMAS, L. et al. High performance bio-based benzoxazine networks from resorcinol and hydroquinone. **European Polymer Journal**, v. 75, p. 486–494, fev. 2016b.

DUMAS, L. et al. Chavicol benzoxazine: Ultrahigh Tg biobased thermoset with tunable extended network. **European Polymer Journal**, v. 81, p. 337–346, ago. 2016c.

ERDOCIA, X. et al. Base catalyzed depolymerization of lignin: Influence of organosolv lignin nature. **Biomass and Bioenergy**, v. 66, p. 379–386, jul. 2014.

FANG, Y. et al. Flame retardant performance of a carbon source containing DOPO derivative in PET and epoxy. **Journal of Applied Polymer Science**, v. 134, n. 12, p. 1–9, 2017.

FAO. **FAO**. Disponível em: http://faostat3.fao.org/faostat-gateway/go/to/browse/Q/QC/E. Acesso em: 28 set. 2018.

FERNÁNDEZ-RODRÍGUEZ, J. et al. Lignin depolymerization for phenolic monomers production by sustainable processes. **Journal of Energy Chemistry**, v. 26, n. 4, p. 622–631, jul. 2017.

FROIMOWICZ, P. et al. Smart, Sustainable, and Ecofriendly Chemical Design of Fully Bio-Based Thermally Stable Thermosets Based on Benzoxazine Chemistry. **ChemSusChem**, v. 9, n. 15, p. 1921–1928, 9 ago. 2016.

FROIMOWICZ, P.; ZHANG, K.; ISHIDA, H. Intramolecular Hydrogen Bonding in Benzoxazines: When Structural Design Becomes Functional. **Chemistry - A European Journal**, v. 22, n. 8, p. 2691–2707, 2016.

FU, T. et al. Inherent flame retardation of semi-aromatic polyesters via binding small-molecule free radicals and charring. **Polymer Chemistry**, v. 7, n. 8, p. 1584–1592, 2016.

GRAMEC SKLEDAR, D.; PETERLIN MAŠIČ, L. Bisphenol A and its analogs: Do their metabolites have endocrine activity? **Environmental Toxicology and Pharmacology**, v. 47, p. 182–199, out. 2016.

HAN, L. et al. Oxazine Ring-Related Vibrational Modes of Benzoxazine Monomers Using Fully Aromatically Substituted, Deuterated, 15 N Isotope Exchanged, and Oxazine-Ring-Substituted Compounds and Theoretical Calculations. **The Journal of Physical Chemistry A**, v. 121, n. 33, p. 6269–6282, 24 ago. 2017.

HARRIS, J. M. (ED.). Poly(Ethylene Glycol) Chemistry. In: **Biotechnical and Biomedical Applications**. Boston, MA: Springer US, 1992.

HASSAN, W. A. W. et al. Examining the influence of bisphenol A on the polymerisation and network properties of an aromatic benzoxazine. **Polymer**, v. 88, p. 52–62, 2016.

HILL, D. J. T. et al. Dynamic mechanical properties of networks prepared from siloxane modified divinyl benzene pre-polymers. **Polymer**, v. 41, n. 26, p. 9131–9137, dez. 2000.

HOLLY, F. W.; COPE, A. C. Condensation Products of Aldehydes and Ketones with o-Aminobenzyl Alcohol and o-Hydroxybenzylamine. **Journal of the American Chemical Society**, v. 66, n. 11, p. 1875–1879, nov. 1944.

HÜLSEY, M. J.; YANG, H.; YAN, N. Sustainable Routes for the Synthesis of Renewable Heteroatom-Containing Chemicals. **ACS Sustainable Chemistry & Engineering**, v. 6, n. 5, p. 5694–5707, 7 maio 2018.

HUNTSMAN. **Benzoxazines**. Disponível em: http://www.huntsman.com/advanced_materials/a/Our Technologies/High Performance Components/Imides and Benzoxazines/Benzoxazines. Acesso em: 22 set. 2018.

IREDALE, R. J.; WARD, C.; HAMERTON, I. Modern advances in bismaleimide resin technology: A 21st century perspective on the chemistry of addition polyimides. **Progress in**

Polymer Science, v. 69, p. 1–21, jun. 2017.

ISHIDA, H.; AGAG, T. Handbook of Benzoxazine Resins. In: ISHIDA, H.; AGAG, T. (Eds.). . **Handbook of Benzoxazine Resins**. Oxford: Elsevier, 2011. p. 712.

ISHIDA, H.; SANDERS, D. P. Improved Thermal and Mechanical Properties of Polybenzoxazines Based on Alkyl-Substituted Aromatic Amines. **Polymer**, v. 38, p. 3289–3301, 2000.

ISIKGOR, F. H.; BECER, C. R. Lignocellulosic biomass: a sustainable platform for the production of bio-based chemicals and polymers. **Polymer Chemistry**, v. 6, n. 25, p. 4497–4559, 2015.

JEENPADIPHAT, S.; MONGKOLPICHAYARAK, I.; TUNGASMITA, D. N. Catechol production from lignin by Al-doped mesoporous silica catalytic cracking. **Journal of Analytical and Applied Pyrolysis**, v. 121, p. 318–328, set. 2016.

KALIAVARADHAN, K.; MUTHUSAMY, S. Synthesis and characterization of various phenylene diamine-based bismaleimide-containing phthalonitrile resins. **Polymer Bulletin**, v. 73, n. 7, p. 1921–1938, 2016.

KAPPE, C. O. Controlled Microwave Heating in Modern Organic Synthesis. **Angewandte Chemie International Edition**, v. 43, n. 46, p. 6250–6284, 26 nov. 2004.

KATHALEWAR, M.; SABNIS, A.; D'MELO, D. Polyurethane coatings prepared from CNSL based polyols: Synthesis, characterization and properties. **Progress in Organic Coatings**, v. 77, n. 3, p. 616–626, 2014.

KHAN, M. A. et al. Experimental and numerical analysis of flexural and impact behaviour of glass/pp sandwich panel for automotive structural applications. **Advanced Composite Materials**, v. 27, n. 4, p. 367–386, 4 jul. 2018.

KOPSIDAS, S.; HAMERTON, I. Examining the thermal behaviour of novel aromatic polybenzoxazine blends containing an organophosphorous compound and polyhedral oligomeric silsesquioxane reagents. **Polymer International**, v. 65, n. 9, p. 1015–1023, set. 2016.

KOTZEBUE, L. R. V. et al. Spectral and thermal studies on the synthesis and catalyzed oligomerization of novel cardanol-based benzoxazines. **Polymer**, v. 92, p. 189–200, 2016.

KOTZEBUE, L. R. V. et al. Development of Fully Biobased High-Performance Bis-Benzoxazine under Environmentally Friendly Conditions. **ACS Sustainable Chemistry & Engineering**, v. 6, n. 4, p. 5485–5494, 2018.

LAURICHESSE, S.; AVÉROUS, L. Chemical modification of lignins: Towards biobased polymers. **Progress in Polymer Science**, v. 39, n. 7, p. 1266–1290, 2014.

LI, B. et al. Preparation of bio-based phenol formaldehyde foams using depolymerized hydrolysis lignin. **Industrial Crops and Products**, v. 97, p. 409–416, mar. 2017.

LI, W. et al. Preparation of novel benzoxazine monomers containing ferrocene moiety and properties of polybenzoxazines. **Polymer**, v. 53, n. 6, p. 1236–1244, 2012.

LIN, C. H. et al. Synthesis of a Bisbenzylideneacetone-Containing Benzoxazine and Its Photo- and Thermally Cured Thermoset. **ACS Omega**, v. 2, n. 7, p. 3432–3440, 2017.

LIU, Y.-L.; CHOU, C.-I. High performance benzoxazine monomers and polymers containing furan groups. **Journal of Polymer Science Part A: Polymer Chemistry**, v. 43, n. 21, p. 5267–5282, 2005.

LLIGADAS, G. et al. Polybenzoxazines: new players in the bio-based polymer arena. **Polym. Chem.**, v. 5, n. 23, p. 6636–6644, 2014.

LOCHAB, B.; VARMA, I. K.; BIJWE, J. Thermal behaviour of cardanol-based benzoxazines. **Journal of Thermal Analysis and Calorimetry**, v. 102, n. 2, p. 769–774, 9 nov. 2010.

LOCHAB, B.; VARMA, I. K.; BIJWE, J. Cardanol-based bisbenzoxazines. **Journal of Thermal Analysis and Calorimetry**, v. 107, n. 2, p. 661–668, 26 ago. 2011.

LOMONACO, D. et al. Thermal studies of new biodiesel antioxidants synthesized from a natural occurring phenolic lipid. **Fuel**, v. 97, p. 552–559, jul. 2012.

LOMONACO, D.; MELE, G.; MAZZETTO, S. E. Cashew Nutshell Liquid (CNSL): From an Agro-industrial Waste to a Sustainable Alternative to Petrochemical Resources. In: ANILKUMAR, P. (Ed.). . **Cashew Nut Shell Liquid**. Zurich: Springer, Cham, 2017. p. 19–38.

MA, R.; GUO, M.; ZHANG, X. Recent advances in oxidative valorization of lignin. **Catalysis Today**, v. 302, p. 50–60, 2018.

MALLAKPOUR, S.; ZADEHNAZARI, A. Improved covalent functionalization of multi-walled carbon nanotubes using ascorbic acid for poly(amide–imide) composites having dopamine linkages. **Bulletin of Materials Science**, v. 40, n. 1, p. 213–222, 2017.

MALLOZZI, M. et al. Endocrine Disrupting Chemicals and Endometrial Cancer: An Overview of Recent Laboratory Evidence and Epidemiological Studies. **International Journal of Environmental Research and Public Health**, v. 14, n. 3, p. 334, 2017.

MAMANPUSH, S. H. et al. Recycled wind turbine blades as a feedstock for second generation composites. **Waste Management**, v. 76, p. 708–714, jun. 2018.

MANIKANNAN, R.; MUTHUSUBRAMANIAN, S. Synthesis and biological activity of 6-alkyl/chloro-3-{4-(6-alkyl/chloro-2H-benzo[e][1,3]oxazin-3(4H)-yl}-3,4-dihydro-2H-benzo[e][1,3]oxazines. **Indian Journal of Chemistry**, v. 49B, n. August, p. 1083–1087, 2010.

MARTINEZ, C. R.; IVERSON, B. L. Rethinking the term “pi-stacking”. **Chemical Science**, v.

3, n. 7, p. 2191–2201, 2012.

MAZZETTO, S. E.; LOMONACO, D. Cashew nut oil: opportunities and challenges in the context of sustainable industrial. **Quimica Nova**, v. 32, n. 3, p. 732–741, 2009.

MENARD, K. P. DYNAMIC MECHANICAL ANALYSIS - A Practical Introduction. In: Boca Raton: CRC Press, 1999. p. 240.

MONISHA, M. et al. Cardanol Benzoxazines: A Versatile Monomer with Advancing Applications. **Macromolecular Chemistry and Physics**, v. 220, n. 3, p. 1800470, 11 fev. 2019.

MOVIL-CABRERA, O. et al. Electrochemical conversion of lignin to useful chemicals. **Biomass and Bioenergy**, v. 88, p. 89–96, maio 2016.

NATARAJAN, M.; MURUGAVEL, S. C. Synthesis, spectral and thermal degradation kinetics of novolac resins derived from cardanol. **High Performance Polymers**, v. 25, n. 6, p. 685–696, 2013.

NG, F. et al. Bio-Based Aromatic Epoxy Monomers for Thermoset Materials. **Molecules**, v. 22, n. 1, p. 149, 18 jan. 2017.

NIELSEN, L. E. Cross-Linking–Effect on Physical Properties of Polymers. **Journal of Macromolecular Science, Part C**, v. 3, n. 1, p. 69–103, 10 jan. 1969.

NING, X.; ISHIDA, H. Phenolic materials via ring-opening polymerization of benzoxazines: Effect of molecular structure on mechanical and dynamic mechanical properties. **Journal of Polymer Science Part B: Polymer Physics**, v. 32, n. 5, p. 921–927, 15 abr. 1994a.

NING, X.; ISHIDA, H. Phenolic materials via ring-opening polymerization: Synthesis and characterization of bisphenol-A based benzoxazines and their polymers. **Journal of Polymer Science Part A: Polymer Chemistry**, v. 32, n. 6, p. 1121–1129, 30 abr. 1994b.

ODIAN, G. **Principles of Polymerization**. 4th. ed. New Jersey: Wiley-Interscience, 2004.

OLIVEIRA, J. R. et al. Microwave-assisted solvent-free synthesis of novel benzoxazines: A faster and environmentally friendly route to the development of bio-based thermosetting resins. **Journal of Polymer Science Part A: Polymer Chemistry**, v. 55, n. 21, p. 3534–3544, 1 nov. 2017.

PERIYASAMY, T.; ASRAFALI, S. P.; KIM, S.-C. Functionalized MWCNTs, an efficient reinforcement for the preparation of eugenol based high performance PBz/BMI/CNT nanocomposites exhibiting outstanding thermo-mechanical properties. **New Journal of Chemistry**, v. 41, n. 14, p. 6607–6615, 2017.

PHALAK, G. A.; PATIL, D. M.; MHASKE, S. T. Synthesis and characterization of thermally curable guaiacol based poly(benzoxazine-urethane) coating for corrosion protection on mild steel. **European Polymer Journal**, v. 88, p. 93–108, mar. 2017.

REISS, G. et al. **Advances in Polymer Synthesis**. New York: Springer US, 1985.

RIBEIRO, F. W. M. et al. Thermal and mechanical analyses of biocomposites from cardanol-based polybenzoxazine and bamboo fibers. **Journal of Thermal Analysis and Calorimetry**, v. 129, n. 1, p. 281–289, 21 jul. 2017.

RODRÍGUEZ, A. M. et al. Influence of Polarity and Activation Energy in Microwave-Assisted Organic Synthesis (MAOS). **ChemistryOpen**, v. 4, n. 3, p. 308–317, jun. 2015.

RUČIGAJ, A.; GRADIŠAR, Š.; KRAJNC, M. Kinetic investigation of a complex curing of the guaiacol bio-based benzoxazine system. **E-Polymers**, v. 16, n. 3, p. 199–206, 2016.

SAHOO, S.; MOHANTY, S.; NAYAK, S. K. Biobased polyurethane adhesive over petroleum based adhesive: Use of renewable resource. **Journal of Macromolecular Science, Part A**, v. 55, n. 1, p. 36–48, 2018.

SAINI, N. K.; AZECHI, M.; ENDO, T. Synthesis and Properties of Spiro-Centered Benzoxazines. **Macromolecules**, v. 48, n. 20, p. 7466–7472, 2015.

SHABESTARI, M. E. et al. Effect of nitrogen and oxygen doped carbon nanotubes on flammability of epoxy nanocomposites. **Carbon**, v. 121, p. 193–200, 2017.

SHARMA, V. et al. Benzoxazine derivatives of phytophenols show anti-plasmodial activity via sodium homeostasis disruption. **Bioorganic & Medicinal Chemistry Letters**, mar. 2018.

SHELDON, R. A. Organic Synthesis - Past, Present and Future. **Chemistry & Industry (London)**, p. 903–906, 1992.

SHELDON, R. A. The E factor 25 years on: the rise of green chemistry and sustainability. **Green Chemistry**, v. 19, n. 1, p. 18–43, 2017.

SHELDON, R. A. Metrics of Green Chemistry and Sustainability: Past, Present, and Future. **ACS Sustainable Chemistry & Engineering**, v. 6, n. 1, p. 32–48, 2 jan. 2018a.

SHELDON, R. A. The Road to Biorenewables: Carbohydrates to Commodity Chemicals. **ACS Sustainable Chemistry & Engineering**, v. 6, n. 4, p. 4464–4480, 2 abr. 2018b.

SHEN, S. B.; ISHIDA, H. Synthesis and characterization of polyfunctional naphthoxazines and related polymers. **Journal of Applied Polymer Science**, v. 61, n. 9, p. 1595–1605, 29 ago. 1996.

SHIKOKU. **Benzoxazine**. Disponível em: http://www.shikoku.co.jp/eng/products/chemical/fine-chemical/benzoxazine.php. Acesso em: 25 set. 2018.

SHUKLA, S. et al. Cardanol benzoxazines – interplay of oxazine functionality (mono to tetra) and properties. **RSC Advances**, v. 5, n. 95, p. 78071–78080, 2015.

SINI, N. K.; BIJWE, J.; VARMA, I. K. Renewable benzoxazine monomer from Vanillin:

Synthesis, characterization, and studies on curing behavior. **Journal of Polymer Science, Part A: Polymer Chemistry**, v. 52, n. 1, p. 7–11, 2014.

SOMISETTI, V. et al. Flexible, hard, and tough biobased polyurethane thermosets from renewable materials: glycerol and 10-undecenoic acid. **Journal of Coatings Technology and Research**, v. 15, n. 1, p. 199–210, 2018.

SPONTÓN, M. et al. Studies on thermal and flame retardant behaviour of mixtures of bis(m-aminophenyl)methylphosphine oxide based benzoxazine and glycidylether or benzoxazine of Bisphenol A. **Polymer Degradation and Stability**, v. 93, n. 12, p. 2158–2165, 2008.

TAKEICHI, T.; KAWAUCHI, T.; AGAG, T. High Performance Polybenzoxazines as a Novel Type of Phenolic Resin. **Polymer Journal**, v. 40, n. 12, p. 1121–1131, 15 dez. 2008.

TEONG, S. P.; YI, G.; ZHANG, Y. Hydroxymethylfurfural production from bioresources: past, present and future. **Green Chemistry**, v. 16, n. 4, p. 2015–2026, 2014.

THIRUKUMARAN, P. et al. Synthesis and characterization of new polybenzoxazines from renewable resources for bio-composite applications. **Polymer Composites**, v. 16, n. 2, p. 1–9, 2014.

TRAN, P.; NGUYEN, Q. T.; LAU, K. T. Fire performance of polymer-based composites for maritime infrastructure. **Composites Part B: Engineering**, v. 155, n. June, p. 31–48, dez. 2018.

TREJO-MACHIN, A. et al. Phloretic acid as an alternative to the phenolation of aliphatic hydroxyls for the elaboration of polybenzoxazine. **Green Chem.**, v. 19, n. 21, p. 5065–5073, 2017.

TRITA, A. S. et al. Synthesis of potential bisphenol A substitutes by isomerising metathesis of renewable raw materials. **Green Chem.**, v. 19, n. 13, p. 3051–3060, 2017.

TROST, B. M. The atom economy - a search for synthetic efficiency. **Science**, v. 254, n. 5037, p. 1471–1477, 1991.

VAFAEEZADEH, M.; HASHEMI, M. M. Polyethylene glycol (PEG) as a green solvent for carbon-carbon bond formation reactions. **Journal of Molecular Liquids**, v. 207, p. 73–79, 2015.

VAN GEMERT, D. et al. Cement concrete and concrete–polymer composites: Two merging worlds. **Cement and Concrete Composites**, v. 27, n. 9–10, p. 926–933, out. 2005.

VAN KREVELEN, D. . Some basic aspects of flame resistance of polymeric materials. **Polymer**, v. 16, n. 8, p. 615–620, ago. 1975.

VINITA, Y. **Yamamoto Vinita**. Disponível em: http://www.vinita.co.jp/en/advanced/technical_information/principle.html. Acesso em: 3 out. 2018.

VOIRIN, C. et al. Functionalization of cardanol: towards biobased polymers and additives. **Polym. Chem.**, v. 5, n. 9, p. 3142–3162, 2014.

WAHYUDIONO; SASAKI, M.; GOTO, M. Recovery of phenolic compounds through the decomposition of lignin in near and supercritical water. **Chemical Engineering and Processing: Process Intensification**, v. 47, n. 9–10, p. 1609–1619, set. 2008.

WANG, C.-F. et al. Low-Surface-Free-Energy Materials Based on Polybenzoxazines. **Angewandte Chemie International Edition**, v. 45, n. 14, p. 2248–2251, 27 mar. 2006a.

WANG, C.-F. et al. Stable Superhydrophobic Polybenzoxazine Surfaces over a Wide pH Range. **Langmuir**, v. 22, n. 20, p. 8289–8292, set. 2006b.

WANG, C. et al. Synthesis and copolymerization of fully bio-based benzoxazines from guaiacol, furfurylamine and stearylamine. **Green Chemistry**, v. 14, n. 10, p. 2799–2806, 2012.

WANG, Y.-X.; ISHIDA, H. Synthesis and Properties of New Thermoplastic Polymers from Substituted 3,4-Dihydro-2 H -1,3-benzoxazines. **Macromolecules**, v. 33, n. 8, p. 2839–2847, abr. 2000.

WANG, Z.; LIU, H.; LIU, S. Low-Dose Bisphenol A Exposure: A Seemingly Instigating Carcinogenic Effect on Breast Cancer. **Advanced Science**, v. 4, n. 2, p. 1600248, 2016.

WENDISCH, V. F.; KIM, Y.; LEE, J.-H. Chemicals from lignin: Recent depolymerization techniques and upgrading extended pathways. **Current Opinion in Green and Sustainable Chemistry**, v. 14, p. 33–39, 2018.

XU, H. et al. Hybrid polybenzoxazine with tunable properties. **RSC Advances**, v. 3, n. 11, p. 3677, 2013.

YAGCI, Y.; KISKAN, B.; GHOSH, N. N. Recent advancement on polybenzoxazine-A newly developed high performance thermoset. **Journal of Polymer Science Part A: Polymer Chemistry**, v. 47, n. 21, p. 5565–5576, 2009.

ZHANG, H. et al. Preparation of superhydrophobic polybenzoxazine/SiO2 films with self-cleaning and ice delay properties. **Progress in Organic Coatings**, v. 123, n. January, p. 254–260, out. 2018.

ZHANG, J. et al. Highly efficient, NiAu-catalyzed hydrogenolysis of lignin into phenolic chemicals. **Green Chem.**, v. 16, n. 5, p. 2432–2437, 2014.

ZHANG, L. et al. Cardanol-capped main-chain benzoxazine oligomers for resin transfer molding. **European Polymer Journal**, v. 93, n. June, p. 284–293, ago. 2017.

ZHU, L.; LI, N.; CHILDS, P. R. N. Light-weighting in aerospace component and system design. **Propulsion and Power Research**, v. 7, n. 2, p. 103–119, jun. 2018.

ZIRBES, M.; WALDVOGEL, S. R. Electro-conversion as sustainable method for the fine chemical production from the biopolymer lignin. **Current Opinion in Green and Sustainable Chemistry**, v. 14, p. 19–25, 2018.

5 CONCLUSION

It was demonstrated that high-performance bio-based benzoxazine monomers from the renewable widely available non-edible starting materials, lignocellulose and Cashew Nut Shell Liquid (CNSL), are interesting alternatives to substitute the commercially available benzoxazines, which use the toxic BPA as starting material.

From lignocellulose derivates, furfurylamine and catechol, the fully bio-based bis-benzoxazine **CT-fu** was obtained, by using an eco-friendly method which used atoxic PEG as solvent and microwave irradiation as a heating source, reducing the reaction time from hours or days to minutes, when compared with traditional heating sources, without compromising the yield. To validate this sustainable method for other benzoxazine resins, the synthesis of bio- and BPA-based benzoxazine **BA-fu** was also successful, showing good potential to apply this method for the production of the already commercially available BPA-based benzoxazine resins. Due to the narrow processing window of **CT-fu**, this monomer was further copolymerized with another benzoxazine **BA-fu** in different ratios, producing polybenzoxazines with elevated thermal and mechanical properties. These polybenzoxazines demonstrated to possess high flame-retardancy with LOI values ranging from 35 to 42 and high glass transition temperatures that ranged from 290 to 350 ºC.

As the bio-based benzoxazine **BA-fu** is still derived from BPA and looking forward to substituting completely BPA as starting material for high-performance benzoxazines, pure technical **CNSL** was chosen to act as the phenolic source for this goal. Using a solvent-free method for **CNSL** with furfurylamine under microwave irradiation, **CNSL-fu** was produced as a low viscous renewable benzoxazine resin. The production of **CNSL-fu** and **CT-fu** are demonstrated to be quite sustainable, not only because of the origin of their starting materials, but also due the greenness of the method of synthesis employed, as determined by the sustainable metrics. Since **CNSL**-based benzoxazines provide usually low thermal and mechanical properties for high-performance polymers, **CNSL-fu** was copolymerized with **CT-fu** into polybenzoxazines that possess these properties. The benzoxazine mixtures that contained 20, 30 and 40 % of **CT-fu** had similar thermal and thermomechanical properties as the commercially available BPA-based benzoxazine **BA-a**, which proofs that **CNSL** and lignocellulose-based chemicals can be used for large scale production of high-performance bio-based benzoxazine resins.

REFERENCES

A. ATTANASI, O. et al. Solvent Free Synthesis of Novel Mono- and Bis-Benzoxazines from Cashew Nut Shell Liquid Components. **Current Organic Chemistry**, v. 16, n. 21, p. 2613–2621, 1 nov. 2012.

AGAG, T.; JIN, L.; ISHIDA, H. A new synthetic approach for difficult benzoxazines: Preparation and polymerization of 4,4′-diaminodiphenyl sulfone-based benzoxazine monomer. **Polymer**, v. 50, n. 25, p. 5940–5944, nov. 2009.

AHMAD, F.; SILVA, E. L.; VARESCHE, M. B. A. Hydrothermal processing of biomass for anaerobic digestion – A review. **Renewable and Sustainable Energy Reviews**, v. 98, n. December 2017, p. 108–124, 2018.

ALTIN KARATAŞ, M.; GÖKKAYA, H. A review on machinability of carbon fiber reinforced polymer (CFRP) and glass fiber reinforced polymer (GFRP) composite materials. **Defence Technology**, v. 14, n. 4, p. 318–326, ago. 2018.

AMARNATH, N.; APPAVOO, D.; LOCHAB, B. Eco-Friendly Halogen-Free Flame Retardant Cardanol Polyphosphazene Polybenzoxazine Networks. **ACS Sustainable Chemistry & Engineering**, v. 6, n. 1, p. 389–402, 2 jan. 2018.

AMBROŽIČ, R.; ŠEBENIK, U.; KRAJNC, M. Synthesis, curing kinetics, thermal and mechanical behavior of novel cardanol-based benzoxazines. **Polymer**, v. 76, p. 203–212, out. 2015.

ANASTAS, P. T.; WARNER, J. C. **Green Chemistry: Theory and Practice**. New York: Oxford University Press, 1998.

BARANEK, A. D. et al. Flexible aliphatic-bridged bisphenol-based polybenzoxazines. **Polymer Chemistry**, v. 3, n. 10, p. 2892–2900, 2012.

BECKHAM, G. T. et al. Opportunities and challenges in biological lignin valorization. **Current Opinion in Biotechnology**, v. 42, n. March, p. 40–53, dez. 2016.

BERESKA, A. et al. The application of organophosphorus flame-retardants in epoxy resin. **Journal of Vinyl and Additive Technology**, v. 23, n. 2, p. 142–151, maio 2017.

BILAL, M. et al. Biotransformation of lignocellulosic materials into value-added products—A review. **International Journal of Biological Macromolecules**, v. 98, p. 447–458, 2017.

BOBADE, S. K. et al. Bio-Based Thermosetting Resins for Future Generation: A Review. **Polymer-Plastics Technology and Engineering**, v. 55, n. 17, p. 1863–1896, 2016.

BOMTEMPO, J.-V.; CHAVES ALVES, F.; DE ALMEIDA OROSKI, F. Developing new platform chemicals: what is required for a new bio-based molecule to become a platform

chemical in the bioeconomy? **Faraday Discuss.**, v. 202, p. 213–225, 2017.

BRADY, J. et al. Developing Solid Oral Dosage Forms. In: QIU, Y. et al. (Eds.). . 2nd. ed. [s.l.] Academic Press, 2017. p. 1176.

BROWN, E. A.; RIDER, D. A. Pegylated Polybenzoxazine Networks with Increased Thermal Stability from Miscible Blends of Tosylated Poly(ethylene glycol) and a Benzoxazine Monomer. **Macromolecules**, v. 50, n. 17, p. 6468–6481, 2017.

BURKE, W. J. 3,4-Dihydro-1,3,2H-Benzoxazines. Reaction of p -Substituted Phenols with N,N-Dimethylolamines. **Journal of the American Chemical Society**, v. 71, n. 2, p. 609–612, fev. 1949.

BURKE, W. J. et al. A New Aminoalkylation Reaction. Condensation of Phenols with Dihydro-1,3-aroxazines. **The Journal of Organic Chemistry**, v. 30, n. 10, p. 3423–3427, 1965.

BURKE, W. J.; GLENNIE, E. L. M.; WEATHERBEE, C. Condensation of Halophenols with Formaldehyde and Primary Amines. **The Journal of Organic Chemistry**, v. 29, n. 4, p. 909–912, 1964.

BURKE, W. J.; MURDOCK, K. C.; EC, G. Condensation of Hydroxyaromatic Compounds with Formaldehyde and Primary Aromatic Amines. **Journal of the American Chemical Society**, v. 76, n. 6, p. 1677–1679, 1954.

BURKE, W. J.; SMITH, R. P.; WEATHERBEE, C. N,N-Bis-(hydroxybenzyl)-amines: Synthesis from Phenols, Formaldehyde and Primary Amines. **Journal of the American Chemical Society**, v. 74, n. 3, p. 602–605, 1952.

BURKE, W. J.; STEPHENS, C. W. Monomeric Products from the Condensation of Phenol with Formaldehyde and Primary Amines. **Journal of the American Chemical Society**, v. 74, n. 6, p. 1518–1520, mar. 1952.

BURKE, W. J.; WEATHERBEE, C. 3,4-Dihydro-1,3,2H-Benzoxazines. Reaction of Polyhydroxybenzenes with N-Methylolamines 1. **Journal of the American Chemical Society**, v. 72, n. 10, p. 4691–4694, out. 1950.

CALÒ, E. et al. Synthesis of a novel cardanol-based benzoxazine monomer and environmentally sustainable production of polymers and bio-composites. **Green Chemistry**, v. 9, n. 7, p. 754–759, 2007.

CHEN, J. et al. Polyethylene glycol and solutions of polyethylene glycol as green reaction media. **Green Chemistry**, v. 7, n. 2, p. 64–82, 2005.

CHEN, Z.; WAN, C. Biological valorization strategies for converting lignin into fuels and chemicals. **Renewable and Sustainable Energy Reviews**, v. 73, p. 610–621, jun. 2017.

CHIU, W.-M. et al. Preparation and characterization of novel polybenzoxazine hybrid materials.

High Performance Polymers, v. 28, n. 8, p. 971–983, 2016.

CHOI, S.-W. et al. Synthesis, characterization and thermal degradation of functional benzoxazine monomers and polymers containing phenylphosphine oxide. **Polymer Degradation and Stability**, v. 91, n. 5, p. 1166–1178, maio 2006.

CINI, E.; PETRICCI, E.; TADDEI, M. Pd/C Catalysis under Microwave Dielectric Heating. **Catalysts**, v. 7, n. 12, p. 89, 20 mar. 2017.

DAI, J. et al. Biobased Benzoxazine Derived from Daidzein and Furfurylamine: Microwave-Assisted Synthesis and Thermal Properties Investigation. **ChemSusChem**, v. 11, n. 18, p. 3175–3183, 21 set. 2018.

DAYO, A. Q. et al. Natural hemp fiber reinforced polybenzoxazine composites: Curing behavior, mechanical and thermal properties. **Composites Science and Technology**, v. 144, p. 114–124, maio 2017.

DE LEON, A. C. et al. High performance polymer nanocomposites for additive manufacturing applications. **Reactive and Functional Polymers**, v. 103, p. 141–155, jun. 2016.

DENG, C. et al. Modes of action of a mono-component intumescent flame retardant MAPP in polyethylene-octene elastomer. **Polymer Degradation and Stability**, v. 138, p. 142–150, 2017.

DHOLAKIYA, B. Unsaturated Polyester Resin for Specialty Applications. In: SALEH, H. E.-D. M. (Ed.). . **Polyester**. Rijeka: InTech, 2012. p. 432.

DOUSE, E. et al. Modification of stress-strain behaviour in aromatic polybenzoxazines using core shell rubbers. **Reactive and Functional Polymers**, v. 103, p. 117–130, jun. 2016.

DRIOWYA, M. et al. **Microwave-assisted synthesis of bioactive six-membered heterocycles and their fused analogues**. [s.l: s.n.]. v. 21

DUMAS, L. et al. Eugenol-based benzoxazine: from straight synthesis to taming of the network properties. **J. Mater. Chem. A**, v. 3, n. 11, p. 6012–6018, 2015.

DUMAS, L. et al. Arbutin-based benzoxazine: en route to an intrinsic water soluble biobased resin. **Green Chem.**, v. 18, n. 18, p. 4954–4960, 2016a.

DUMAS, L. et al. High performance bio-based benzoxazine networks from resorcinol and hydroquinone. **European Polymer Journal**, v. 75, p. 486–494, fev. 2016b.

DUMAS, L. et al. Chavicol benzoxazine: Ultrahigh Tg biobased thermoset with tunable extended network. **European Polymer Journal**, v. 81, p. 337–346, ago. 2016c.

ERDOCIA, X. et al. Base catalyzed depolymerization of lignin: Influence of organosolv lignin nature. **Biomass and Bioenergy**, v. 66, p. 379–386, jul. 2014.

FANG, Y. et al. Flame retardant performance of a carbon source containing DOPO derivative in PET and epoxy. **Journal of Applied Polymer Science**, v. 134, n. 12, p. 1–9, 2017.

FAO. **FAO**. Disponível em: http://faostat3.fao.org/faostat-gateway/go/to/browse/Q/QC/E. Acesso em: 28 set. 2018.

FERNÁNDEZ-RODRÍGUEZ, J. et al. Lignin depolymerization for phenolic monomers production by sustainable processes. **Journal of Energy Chemistry**, v. 26, n. 4, p. 622–631, jul. 2017.

FROIMOWICZ, P. et al. Smart, Sustainable, and Ecofriendly Chemical Design of Fully Bio-Based Thermally Stable Thermosets Based on Benzoxazine Chemistry. **ChemSusChem**, v. 9, n. 15, p. 1921–1928, 9 ago. 2016.

FROIMOWICZ, P.; ZHANG, K.; ISHIDA, H. Intramolecular Hydrogen Bonding in Benzoxazines: When Structural Design Becomes Functional. **Chemistry - A European Journal**, v. 22, n. 8, p. 2691–2707, 2016.

FU, T. et al. Inherent flame retardation of semi-aromatic polyesters via binding small-molecule free radicals and charring. **Polymer Chemistry**, v. 7, n. 8, p. 1584–1592, 2016.

GAO, Y. et al. Unsaturated polyester resin concrete: A review. **Construction and Building Materials**, v. 228, p. 116709, 2019.

GRAMEC SKLEDAR, D.; PETERLIN MAŠIČ, L. Bisphenol A and its analogs: Do their metabolites have endocrine activity? **Environmental Toxicology and Pharmacology**, v. 47, p. 182–199, out. 2016.

HAN, L. et al. Oxazine Ring-Related Vibrational Modes of Benzoxazine Monomers Using Fully Aromatically Substituted, Deuterated, 15 N Isotope Exchanged, and Oxazine-Ring-Substituted Compounds and Theoretical Calculations. **The Journal of Physical Chemistry A**, v. 121, n. 33, p. 6269–6282, 24 ago. 2017.

HARRIS, J. M. (ED.). Poly(Ethylene Glycol) Chemistry. In: **Biotechnical and Biomedical Applications**. Boston, MA: Springer US, 1992.

HASSAN, W. A. W. et al. Examining the influence of bisphenol A on the polymerisation and network properties of an aromatic benzoxazine. **Polymer**, v. 88, p. 52–62, 2016.

HILL, D. J. T. et al. Dynamic mechanical properties of networks prepared from siloxane modified divinyl benzene pre-polymers. **Polymer**, v. 41, n. 26, p. 9131–9137, dez. 2000.

HOLLY, F. W.; COPE, A. C. Condensation Products of Aldehydes and Ketones with o-Aminobenzyl Alcohol and o-Hydroxybenzylamine. **Journal of the American Chemical Society**, v. 66, n. 11, p. 1875–1879, nov. 1944.

HÜLSEY, M. J.; YANG, H.; YAN, N. Sustainable Routes for the Synthesis of Renewable

Heteroatom-Containing Chemicals. **ACS Sustainable Chemistry & Engineering**, v. 6, n. 5, p. 5694–5707, 7 maio 2018.

HUNTSMAN. **Benzoxazines**. Disponível em: http://www.huntsman.com/advanced_materials/a/Our Technologies/High Performance Components/Imides and Benzoxazines/Benzoxazines. Acesso em: 22 set. 2018.

IREDALE, R. J.; WARD, C.; HAMERTON, I. Modern advances in bismaleimide resin technology: A 21st century perspective on the chemistry of addition polyimides. **Progress in Polymer Science**, v. 69, p. 1–21, jun. 2017.

ISHIDA, H.; AGAG, T. Handbook of Benzoxazine Resins. In: ISHIDA, H.; AGAG, T. (Eds.). . **Handbook of Benzoxazine Resins**. Oxford: Elsevier, 2011. p. 712.

ISHIDA, H.; SANDERS, D. P. Improved Thermal and Mechanical Properties of Polybenzoxazines Based on Alkyl-Substituted Aromatic Amines. **Polymer**, v. 38, p. 3289–3301, 2000.

ISIKGOR, F. H.; BECER, C. R. Lignocellulosic biomass: a sustainable platform for the production of bio-based chemicals and polymers. **Polymer Chemistry**, v. 6, n. 25, p. 4497–4559, 2015.

JEENPADIPHAT, S.; MONGKOLPICHAYARAK, I.; TUNGASMITA, D. N. Catechol production from lignin by Al-doped mesoporous silica catalytic cracking. **Journal of Analytical and Applied Pyrolysis**, v. 121, p. 318–328, set. 2016.

KALIAVARADHAN, K.; MUTHUSAMY, S. Synthesis and characterization of various phenylene diamine-based bismaleimide-containing phthalonitrile resins. **Polymer Bulletin**, v. 73, n. 7, p. 1921–1938, 2016.

KAPPE, C. O. Controlled Microwave Heating in Modern Organic Synthesis. **Angewandte Chemie International Edition**, v. 43, n. 46, p. 6250–6284, 26 nov. 2004.

KATHALEWAR, M.; SABNIS, A.; D’MELO, D. Polyurethane coatings prepared from CNSL based polyols: Synthesis, characterization and properties. **Progress in Organic Coatings**, v. 77, n. 3, p. 616–626, 2014.

KHAN, M. A. et al. Experimental and numerical analysis of flexural and impact behaviour of glass/pp sandwich panel for automotive structural applications. **Advanced Composite Materials**, v. 27, n. 4, p. 367–386, 4 jul. 2018.

KISKAN, B. Adapting benzoxazine chemistry for unconventional applications. **Reactive and Functional Polymers**, v. 129, p. 76–88, ago. 2018.

KISKAN, B.; GHOSH, N. N.; YAGCI, Y. Polybenzoxazine-based composites as high-performance materials. **Polymer International**, v. 60, n. 2, p. 167–177, fev. 2011.

KOPSIDAS, S.; HAMERTON, I. Examining the thermal behaviour of novel aromatic polybenzoxazine blends containing an organophosphorous compound and polyhedral oligomeric silsesquioxane reagents. **Polymer International**, v. 65, n. 9, p. 1015–1023, set. 2016.

KOTZEBUE, L. R. V. et al. Spectral and thermal studies on the synthesis and catalyzed oligomerization of novel cardanol-based benzoxazines. **Polymer**, v. 92, p. 189–200, 2016.

KOTZEBUE, L. R. V. et al. Development of Fully Biobased High-Performance Bis-Benzoxazine under Environmentally Friendly Conditions. **ACS Sustainable Chemistry & Engineering**, v. 6, n. 4, p. 5485–5494, 2018.

LAURICHESSE, S.; AVÉROUS, L. Chemical modification of lignins: Towards biobased polymers. **Progress in Polymer Science**, v. 39, n. 7, p. 1266–1290, 2014.

LI, B. et al. Preparation of bio-based phenol formaldehyde foams using depolymerized hydrolysis lignin. **Industrial Crops and Products**, v. 97, p. 409–416, mar. 2017.

LI, W. et al. Preparation of novel benzoxazine monomers containing ferrocene moiety and properties of polybenzoxazines. **Polymer**, v. 53, n. 6, p. 1236–1244, 2012.

LIN, C. H. et al. Synthesis of a Bisbenzylideneacetone-Containing Benzoxazine and Its Photo- and Thermally Cured Thermoset. **ACS Omega**, v. 2, n. 7, p. 3432–3440, 2017.

LIU, Y.-L.; CHOU, C.-I. High performance benzoxazine monomers and polymers containing furan groups. **Journal of Polymer Science Part A: Polymer Chemistry**, v. 43, n. 21, p. 5267–5282, 2005.

LLIGADAS, G. et al. Polybenzoxazines: new players in the bio-based polymer arena. **Polym. Chem.**, v. 5, n. 23, p. 6636–6644, 2014.

LOCHAB, B.; VARMA, I. K.; BIJWE, J. Thermal behaviour of cardanol-based benzoxazines. **Journal of Thermal Analysis and Calorimetry**, v. 102, n. 2, p. 769–774, 9 nov. 2010.

LOCHAB, B.; VARMA, I. K.; BIJWE, J. Cardanol-based bisbenzoxazines. **Journal of Thermal Analysis and Calorimetry**, v. 107, n. 2, p. 661–668, 26 ago. 2011.

LOMONACO, D. et al. Thermal studies of new biodiesel antioxidants synthesized from a natural occurring phenolic lipid. **Fuel**, v. 97, p. 552–559, jul. 2012.

LOMONACO, D.; MELE, G.; MAZZETTO, S. E. Cashew Nutshell Liquid (CNSL): From an Agro-industrial Waste to a Sustainable Alternative to Petrochemical Resources. In: ANILKUMAR, P. (Ed.). . **Cashew Nut Shell Liquid**. Zurich: Springer, Cham, 2017. p. 19–38.

LYU, Y.; ISHIDA, H. Natural-sourced benzoxazine resins, homopolymers, blends and composites: A review of their synthesis, manufacturing and applications. **Progress in Polymer Science**, v. 99, p. 101168, dez. 2019.

MA, R.; GUO, M.; ZHANG, X. Recent advances in oxidative valorization of lignin. **Catalysis Today**, v. 302, p. 50–60, 2018.

MALLAKPOUR, S.; ZADEHNAZARI, A. Improved covalent functionalization of multi-walled carbon nanotubes using ascorbic acid for poly(amide–imide) composites having dopamine linkages. **Bulletin of Materials Science**, v. 40, n. 1, p. 213–222, 2017.

MALLOZZI, M. et al. Endocrine Disrupting Chemicals and Endometrial Cancer: An Overview of Recent Laboratory Evidence and Epidemiological Studies. **International Journal of Environmental Research and Public Health**, v. 14, n. 3, p. 334, 2017.

MAMANPUSH, S. H. et al. Recycled wind turbine blades as a feedstock for second generation composites. **Waste Management**, v. 76, p. 708–714, jun. 2018.

MANIKANNAN, R.; MUTHUSUBRAMANIAN, S. Synthesis and biological activity of 6-alkyl/chloro-3-{4-(6-alkyl/chloro-2H-benzo[e][1,3]oxazin-3(4H)-yl}-3,4-dihydro-2H-benzo[e][1,3]oxazines. **Indian Journal of Chemistry**, v. 49B, n. August, p. 1083–1087, 2010.

MARTINEZ, C. R.; IVERSON, B. L. Rethinking the term "pi-stacking". **Chemical Science**, v. 3, n. 7, p. 2191–2201, 2012.

MAZZETTO, S. E.; LOMONACO, D. Cashew nut oil: opportunities and challenges in the context of sustainable industrial. **Quimica Nova**, v. 32, n. 3, p. 732–741, 2009.

MENARD, K. P. DYNAMIC MECHANICAL ANALYSIS - A Practical Introduction. In: Boca Raton: CRC Press, 1999. p. 240.

MONISHA, M. et al. Cardanol Benzoxazines: A Versatile Monomer with Advancing Applications. **Macromolecular Chemistry and Physics**, v. 220, n. 3, p. 1800470, 11 fev. 2019.

MOVIL-CABRERA, O. et al. Electrochemical conversion of lignin to useful chemicals. **Biomass and Bioenergy**, v. 88, p. 89–96, maio 2016.

NAIR, C. Advances in addition-cure phenolic resins. **Progress in Polymer Science**, v. 29, n. 5, p. 401–498, maio 2004.

NAIR, V.; VINU, R. Production of guaiacols via catalytic fast pyrolysis of alkali lignin using titania, zirconia and ceria. **Journal of Analytical and Applied Pyrolysis**, v. 119, p. 31–39, maio 2016.

NATARAJAN, M.; MURUGAVEL, S. C. Synthesis, spectral and thermal degradation kinetics of novolac resins derived from cardanol. **High Performance Polymers**, v. 25, n. 6, p. 685–696, 2013.

NG, F. et al. Bio-Based Aromatic Epoxy Monomers for Thermoset Materials. **Molecules**, v. 22, n. 1, p. 149, 18 jan. 2017.

NIELSEN, L. E. Cross-Linking–Effect on Physical Properties of Polymers. **Journal of Macromolecular Science, Part C**, v. 3, n. 1, p. 69–103, 10 jan. 1969.

NING, X.; ISHIDA, H. Phenolic materials via ring-opening polymerization of benzoxazines: Effect of molecular structure on mechanical and dynamic mechanical properties. **Journal of Polymer Science Part B: Polymer Physics**, v. 32, n. 5, p. 921–927, 15 abr. 1994a.

NING, X.; ISHIDA, H. Phenolic materials via ring-opening polymerization: Synthesis and characterization of bisphenol-A based benzoxazines and their polymers. **Journal of Polymer Science Part A: Polymer Chemistry**, v. 32, n. 6, p. 1121–1129, 30 abr. 1994b.

ODIAN, G. **Principles of Polymerization**. 4th. ed. New Jersey: Wiley-Interscience, 2004.

OLIVEIRA, J. R. et al. Microwave-assisted solvent-free synthesis of novel benzoxazines: A faster and environmentally friendly route to the development of bio-based thermosetting resins. **Journal of Polymer Science Part A: Polymer Chemistry**, v. 55, n. 21, p. 3534–3544, 1 nov. 2017.

PERIYASAMY, T.; ASRAFALI, S. P.; KIM, S.-C. Functionalized MWCNTs, an efficient reinforcement for the preparation of eugenol based high performance PBz/BMI/CNT nanocomposites exhibiting outstanding thermo-mechanical properties. **New Journal of Chemistry**, v. 41, n. 14, p. 6607–6615, 2017.

PHALAK, G. A.; PATIL, D. M.; MHASKE, S. T. Synthesis and characterization of thermally curable guaiacol based poly(benzoxazine-urethane) coating for corrosion protection on mild steel. **European Polymer Journal**, v. 88, p. 93–108, mar. 2017.

RAQUEZ, J.-M. et al. Thermosetting (bio)materials derived from renewable resources: A critical review. **Progress in Polymer Science**, v. 35, n. 4, p. 487–509, abr. 2010.

REISS, G. et al. **Advances in Polymer Synthesis**. New York: Springer US, 1985.

RIBEIRO, F. W. M. et al. Thermal and mechanical analyses of biocomposites from cardanol-based polybenzoxazine and bamboo fibers. **Journal of Thermal Analysis and Calorimetry**, v. 129, n. 1, p. 281–289, 21 jul. 2017.

RODRÍGUEZ, A. M. et al. Influence of Polarity and Activation Energy in Microwave-Assisted Organic Synthesis (MAOS). **ChemistryOpen**, v. 4, n. 3, p. 308–317, jun. 2015.

RUČIGAJ, A.; GRADIŠAR, Š.; KRAJNC, M. Kinetic investigation of a complex curing of the guaiacol bio-based benzoxazine system. **E-Polymers**, v. 16, n. 3, p. 199–206, 2016.

SAHOO, S.; MOHANTY, S.; NAYAK, S. K. Biobased polyurethane adhesive over petroleum based adhesive: Use of renewable resource. **Journal of Macromolecular Science, Part A**, v. 55, n. 1, p. 36–48, 2018.

SAINI, N. K.; AZECHI, M.; ENDO, T. Synthesis and Properties of Spiro-Centered

Benzoxazines. **Macromolecules**, v. 48, n. 20, p. 7466–7472, 2015.

SARIKA, P. R. et al. Bio-Based Alternatives to Phenol and Formaldehyde for the Production of Resins. **Polymers**, v. 12, n. 10, p. 2237, 28 set. 2020.

SHABESTARI, M. E. et al. Effect of nitrogen and oxygen doped carbon nanotubes on flammability of epoxy nanocomposites. **Carbon**, v. 121, p. 193–200, 2017.

SHARMA, V. et al. Benzoxazine derivatives of phytophenols show anti-plasmodial activity via sodium homeostasis disruption. **Bioorganic & Medicinal Chemistry Letters**, mar. 2018.

SHELDON, R. A. Organic Synthesis - Past, Present and Future. **Chemistry & Industry (London)**, p. 903–906, 1992.

SHELDON, R. A. The E factor 25 years on: the rise of green chemistry and sustainability. **Green Chemistry**, v. 19, n. 1, p. 18–43, 2017.

SHELDON, R. A. Metrics of Green Chemistry and Sustainability: Past, Present, and Future. **ACS Sustainable Chemistry & Engineering**, v. 6, n. 1, p. 32–48, 2 jan. 2018a.

SHELDON, R. A. The Road to Biorenewables: Carbohydrates to Commodity Chemicals. **ACS Sustainable Chemistry & Engineering**, v. 6, n. 4, p. 4464–4480, 2 abr. 2018b.

SHEN, S. B.; ISHIDA, H. Synthesis and characterization of polyfunctional naphthoxazines and related polymers. **Journal of Applied Polymer Science**, v. 61, n. 9, p. 1595–1605, 29 ago. 1996.

SHIKOKU. **Benzoxazine**. Disponível em: http://www.shikoku.co.jp/eng/products/chemical/fine-chemical/benzoxazine.php. Acesso em: 25 set. 2018.

SHUKLA, S. et al. Cardanol benzoxazines – interplay of oxazine functionality (mono to tetra) and properties. **RSC Advances**, v. 5, n. 95, p. 78071–78080, 2015.

SINI, N. K.; BIJWE, J.; VARMA, I. K. Renewable benzoxazine monomer from Vanillin: Synthesis, characterization, and studies on curing behavior. **Journal of Polymer Science, Part A: Polymer Chemistry**, v. 52, n. 1, p. 7–11, 2014.

SOMISETTI, V. et al. Flexible, hard, and tough biobased polyurethane thermosets from renewable materials: glycerol and 10-undecenoic acid. **Journal of Coatings Technology and Research**, v. 15, n. 1, p. 199–210, 2018.

SPONTÓN, M. et al. Studies on thermal and flame retardant behaviour of mixtures of bis(m-aminophenyl)methylphosphine oxide based benzoxazine and glycidylether or benzoxazine of Bisphenol A. **Polymer Degradation and Stability**, v. 93, n. 12, p. 2158–2165, 2008.

TAKEICHI, T.; KAWAUCHI, T.; AGAG, T. High Performance Polybenzoxazines as a Novel Type of Phenolic Resin. **Polymer Journal**, v. 40, n. 12, p. 1121–1131, 15 dez. 2008.

TEONG, S. P.; YI, G.; ZHANG, Y. Hydroxymethylfurfural production from bioresources: past, present and future. **Green Chemistry**, v. 16, n. 4, p. 2015–2026, 2014.

THIRUKUMARAN, P. et al. Synthesis and characterization of new polybenzoxazines from renewable resources for bio-composite applications. **Polymer Composites**, v. 16, n. 2, p. 1–9, 2014.

TRAN, P.; NGUYEN, Q. T.; LAU, K. T. Fire performance of polymer-based composites for maritime infrastructure. **Composites Part B: Engineering**, v. 155, n. June, p. 31–48, dez. 2018.

TREJO-MACHIN, A. et al. Phloretic acid as an alternative to the phenolation of aliphatic hydroxyls for the elaboration of polybenzoxazine. **Green Chem.**, v. 19, n. 21, p. 5065–5073, 2017.

TRITA, A. S. et al. Synthesis of potential bisphenol A substitutes by isomerising metathesis of renewable raw materials. **Green Chem.**, v. 19, n. 13, p. 3051–3060, 2017.

TROST, B. M. The atom economy - a search for synthetic efficiency. **Science**, v. 254, n. 5037, p. 1471–1477, 1991.

VAFAEEZADEH, M.; HASHEMI, M. M. Polyethylene glycol (PEG) as a green solvent for carbon-carbon bond formation reactions. **Journal of Molecular Liquids**, v. 207, p. 73–79, 2015.

VAN GEMERT, D. et al. Cement concrete and concrete–polymer composites: Two merging worlds. **Cement and Concrete Composites**, v. 27, n. 9–10, p. 926–933, out. 2005.

VAN KREVELEN, D. . Some basic aspects of flame resistance of polymeric materials. **Polymer**, v. 16, n. 8, p. 615–620, ago. 1975.

VERMA, C. et al. Epoxy resins as anticorrosive polymeric materials: A review. **Reactive and Functional Polymers**, v. 156, p. 104741, nov. 2020.

VINITA, Y. **Yamamoto Vinita**. Disponível em: http://www.vinita.co.jp/en/advanced/technical_information/principle.html. Acesso em: 3 out. 2018.

VOIRIN, C. et al. Functionalization of cardanol: towards biobased polymers and additives. **Polym. Chem.**, v. 5, n. 9, p. 3142–3162, 2014.

WAHYUDIONO; SASAKI, M.; GOTO, M. Recovery of phenolic compounds through the decomposition of lignin in near and supercritical water. **Chemical Engineering and Processing: Process Intensification**, v. 47, n. 9–10, p. 1609–1619, set. 2008.

WANG, C.-F. et al. Low-Surface-Free-Energy Materials Based on Polybenzoxazines. **Angewandte Chemie International Edition**, v. 45, n. 14, p. 2248–2251, 27 mar. 2006a.

WANG, C.-F. et al. Stable Superhydrophobic Polybenzoxazine Surfaces over a Wide pH Range.

Langmuir, v. 22, n. 20, p. 8289–8292, set. 2006b.

WANG, C. et al. Synthesis and copolymerization of fully bio-based benzoxazines from guaiacol, furfurylamine and stearylamine. **Green Chemistry**, v. 14, n. 10, p. 2799–2806, 2012.

WANG, Y.-X.; ISHIDA, H. Synthesis and Properties of New Thermoplastic Polymers from Substituted 3,4-Dihydro-2 H -1,3-benzoxazines. **Macromolecules**, v. 33, n. 8, p. 2839–2847, abr. 2000.

WANG, Z.; LIU, H.; LIU, S. Low-Dose Bisphenol A Exposure: A Seemingly Instigating Carcinogenic Effect on Breast Cancer. **Advanced Science**, v. 4, n. 2, p. 1600248, 2016.

WENDISCH, V. F.; KIM, Y.; LEE, J.-H. Chemicals from lignin: Recent depolymerization techniques and upgrading extended pathways. **Current Opinion in Green and Sustainable Chemistry**, v. 14, p. 33–39, 2018.

XU, H. et al. Hybrid polybenzoxazine with tunable properties. **RSC Advances**, v. 3, n. 11, p. 3677, 2013.

XU, Y. et al. Research status, industrial application demand and prospects of phenolic resin. **RSC Advances**, v. 9, n. 50, p. 28924–28935, 2019.

YAGCI, Y.; KISKAN, B.; GHOSH, N. N. Recent advancement on polybenzoxazine-A newly developed high performance thermoset. **Journal of Polymer Science Part A: Polymer Chemistry**, v. 47, n. 21, p. 5565–5576, 2009.

ZHANG, H. et al. Preparation of superhydrophobic polybenzoxazine/SiO2 films with self-cleaning and ice delay properties. **Progress in Organic Coatings**, v. 123, n. January, p. 254–260, out. 2018.

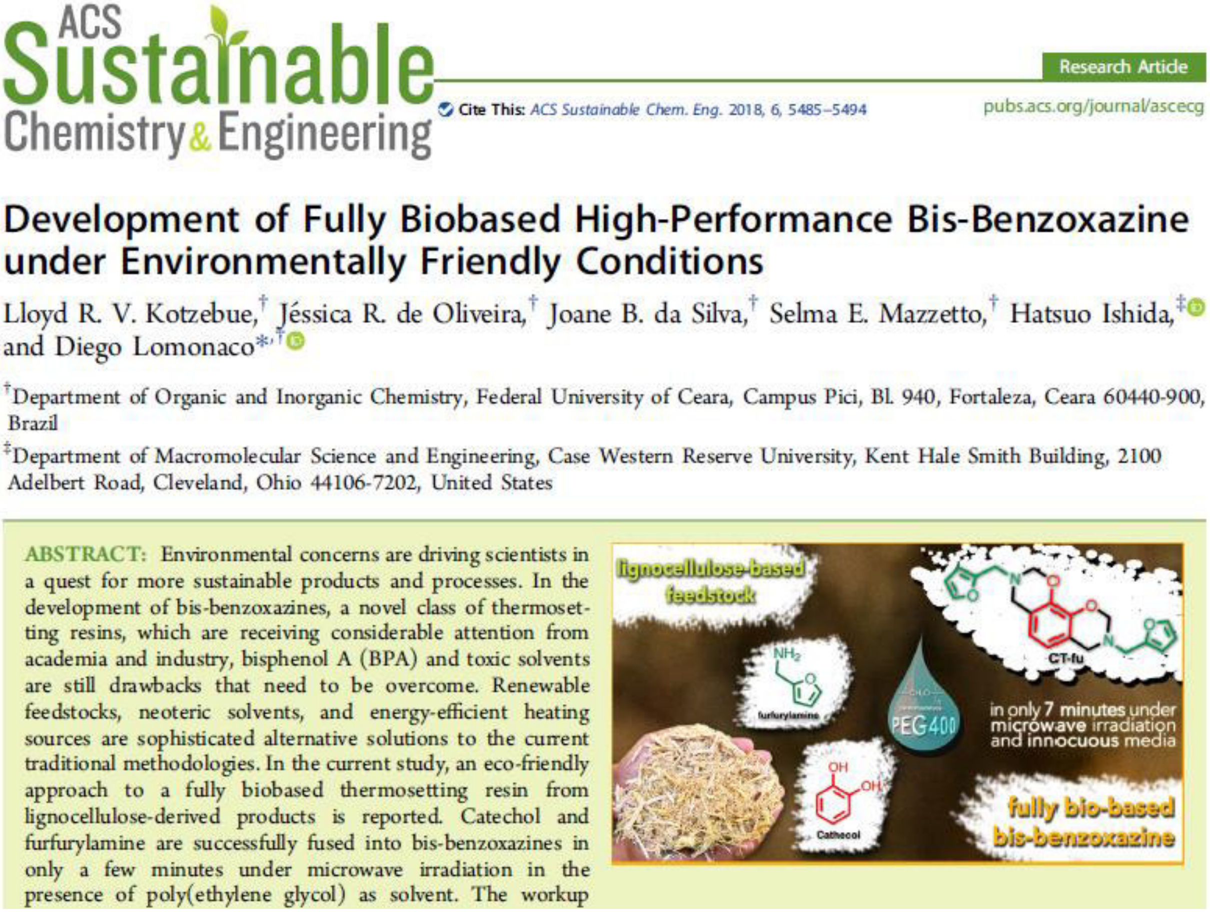
ZHANG, J. et al. Highly efficient, NiAu-catalyzed hydrogenolysis of lignin into phenolic chemicals. **Green Chem.**, v. 16, n. 5, p. 2432–2437, 2014.

ZHANG, L. et al. Cardanol-capped main-chain benzoxazine oligomers for resin transfer molding. **European Polymer Journal**, v. 93, n. June, p. 284–293, ago. 2017.

ZHU, L.; LI, N.; CHILDS, P. R. N. Light-weighting in aerospace component and system design. **Propulsion and Power Research**, v. 7, n. 2, p. 103–119, jun. 2018.

ZIRBES, M.; WALDVOGEL, S. R. Electro-conversion as sustainable method for the fine chemical production from the biopolymer lignin. **Current Opinion in Green and Sustainable Chemistry**, v. 14, p. 19–25, 2018.

ATTACHEMENT A – DEVELOPMENT OF FULLY BIO-BASED HIGH-PERFORMANCE BIS-BENZOXAZINE UNDER ENVIRONMENTALLY FRIENDLY CONDITIONS



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Development of Fully Biobased High-Performance Bis-Benzoxazine under Environmentally Friendly Conditions

Lloyd R. V. Kotzebue,[†] Jéssica R. de Oliveira,[†] Joane B. da Silva,[†] Selma E. Mazzetto,[†] Hatsuo Ishida,[‡] and Diego Lomonaco*[,†]

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ABSTRACT: Environmental concerns are driving scientists in a quest for more sustainable products and processes. In the development of bis-benzoxazines, a novel class of thermosetting resins, which are receiving considerable attention from academia and industry, bisphenol A (BPA) and toxic solvents are still drawbacks that need to be overcome. Renewable feedstocks, neoteric solvents, and energy-efficient heating sources are sophisticated alternative solutions to the current traditional methodologies. In the current study, an eco-friendly approach to a fully biobased thermosetting resin from lignocellulose-derived products is reported. Catechol and furfurylamine are successfully fused into bis-benzoxazines in only a few minutes under microwave irradiation in the presence of poly(ethylene glycol) as solvent. The workup

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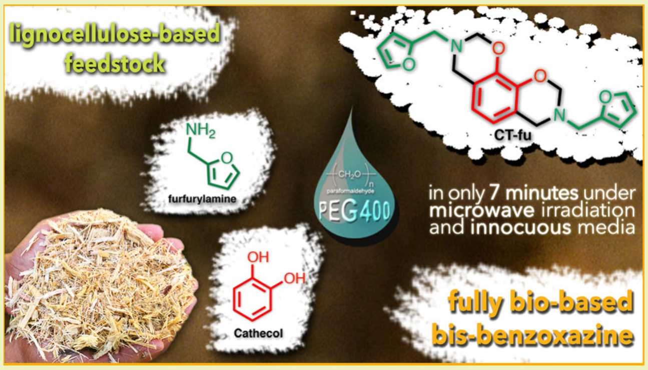

KEYWORDS: *Catechol, Polybenzoxazines, Poly(ethylene glycol), Microwave-assisted synthesis, Green chemistry*

■ INTRODUCTION

Thermosetting resins are key players in the advanced materials sector. Due to their high modulus, strength, durability, and thermal and chemical resistances, thermosets provide high-performance products for industry. The most commonly used networks are phenolics, epoxy and polyester, especially in fields like civil infrastructure and transportation.[1]

More recently, a novel class of commercial available thermosetting compounds, based on an aromatic oxazine ring, or benzoxazines, is being reported as a modern alternative for those classic resins.[2]

When exposed to elevated temperature, benzoxazine monomers start to polymerize into polybenzoxazines, through a ring-opening polymerization (ROP) process, which does not require initiators or release byproducts.[3−5]

Polybenzoxazines are now receiving a considerable attention from academia and industry, since they present outstanding characteristics, such as near-zero shrinkage upon polymerization, high glass-transition temperature (T_g), excellent thermal and mechanical properties, flame retardancy, and low surface energy.[6−9]

Another interesting aspect of benzoxazine resins is their great versatile synthetic routes. Since it uses a phenolic compound, a primary amine and formaldehyde as starting materials, a wide range of reactants can be employed. Depending on the starting materials, the property of such resins, and hence of their polymers, can be tailored for the required applications.[10−14]

Bisphenol A (BPA)-based benzoxazine is considered a standard due to easy availability in high purity and inexpensive nature of BPA. BPA is one of the highest-volume monomers currently produced, on about 4.5 million tons per annum scale, but has been raising many health concerns due to its endocrine activities in humans.[15] An increasing number of recent studies have shown that even BPA alternatives, like bisphenol S (BPS) and bisphenol F (BPF), present comparable effects on the endocrine system as BPA itself.[16]

For bis-benzoxazines synthesis, an organic solvent is generally required to overcome technical restrictions, e.g., high viscosity, high melting points, or poor solubility of reactants. Furthermore, the commonly used solvents are toxic, such as toluene, *p*-xylene, or dioxane, are toxic. It is also usual

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for the reaction time of these procedures to last for hours or even days under traditional heating.[11,17]

Not only health but also environmental concerns are driving scientists and researchers in a quest to replace traditional petroleum-derived chemicals and materials. In the contemporary society, novel processes and products must be designed aiming not only their immediate applications, but also incorporating their footprints for future generations. With the advent of "green chemistry", Anastas and Warner provided a guidance to help chemists in achieving this goal.[18] On the basis of these principles, sophisticated approaches to overcome these barriers could include the use of (i) renewable feedstock (e.g., biomass residues); (ii) neoteric solvents (e.g., ionic liquids (IL) or polyethylene glycol (PEG)); and (iii) more energy-efficient heating sources, like microwave irradiation.

Many attempts have been made toward sustainable development of benzoxazines. The utilization of biobased renewable feedstock has allowed emergence of many novel and promising benzoxazine monomers through the exploration of both biomass-derived building blocks: phenols and amines.[19]

Furfurylamine (fu), or 2-(aminomethyl)furan, is an example of a biobased amine that makes possible the synthesis of eco-friendly benzoxazines, generating polymers with excellent properties.[20] Furfurylamine can be easily obtained from furfural, which is a well-known platform chemical produced on industrial scales from the decomposition of carbohydrate materials and listed as the top 10 value-added biobased chemicals by the US Department of Energy.[21]

Several naturally occurring phenolic compounds have also been reported as alternatives to BPA. Cardanol,[22−24] urushiol,[25] vanillin,[26] guaiacol,[27] eugenol,[28] and coumarins[8] were thoroughly studied as starting materials for the synthesis of benzoxazine monomers and converted into polybenzoxazines.

Nevertheless, to the best of our knowledge, there are still no reports in the scientific literature on the synthesis of bis-benzoxazines starting from catechol (**CT**). Chemically described as 1,2-dihydroxybenzene, **CT** is a renewable raw material that can be obtained from lignin by different chemical processes.[29−31] Recent results published by Dumas and coworkers, addressing the synthesis of bis-benzoxazines based on resorcinol and hydroquinone,[10] indicate catechol as a promising alternative renewable starting material for the synthesis of high-performance polymers.

In the case of neoteric solvents, poly(ethylene glycol) (PEG) was already employed as a reactant in previous syntheses of benzoxazines,[32,33] but not as an inert and innocuous reaction media. Being a nontoxic polyether compound, which is available commercially in a variety of molecular weights and has been approved by U.S. Food and Drug Administration (FDA) for internal consumption,[34] PEG has unique properties that turns it in an idiosyncratic alternative to traditional organic solvents. They are biodegradable, nonvolatile, low flammability, highly stable to acid, base and high temperatures; may be recovered by extraction or by direct distillation; and are soluble in polar and nonpolar solvents, but insoluble in aliphatic hydrocarbons.[35,36] Another important peculiarity is its high capacity to absorb microwave (MW) radiation.[37,38] In microwave-assisted organic synthesis (MAOS), which uses microwave irradiation as heating source due to the effective heating of certain materials (reactants or solvent) by the "microwave dielectric heating effects", it is possible to drastically reduce reaction time, decrease byproduct formation and, consequently, increase product purity.[39]

On the basis of the above, we report the microwave-assisted synthesis of a fully biobased bis-benzoxazine, starting from two lignocellulose-based bioproducts, catechol and furfurylamine, having PEG as solvent. In order to extend this methodological procedure for more frequently employed phenols, the well-known BPA was also evaluated as a control under these new conditions. The obtained monomers were structurally characterized by Fourier transform infrared spectroscopy (FTIR), and ^{1}H and ^{13}C nuclear magnetic resonance spectroscopy (NMR). In view of the great potential of bis-benzoxazines in the development of high-performance materials, the thermal behaviors of these monomers were also investigated by differential scanning calorimetry (DSC). After spectral and thermal characterization, their copolymers were analyzed by thermogravimetric analysis (TGA) and dynamic mechanical analysis (DMA).

■ EXPERIMENTAL SECTION

Materials and Methods. Catechol (99%), bisphenol A (97%), furfurylamine (99%), and paraformaldehyde (95%) were used as-received by Sigma-Aldrich without any purification. Poly(ethylene glycol) (PEG) (Kollisolv PEG E 400) of M_n = 400 Da was used as-received by Aldrich.

Analytical Methods. *^{13}C and ^{1}H Nuclear Magnetic Resonance Spectroscopy (^{1}H NMR and ^{13}C NMR).* The ^{1}H NMR and ^{13}C NMR spectra were recorded on a BRUKER spectrometer, model Avance DPX, operating at 300 MHz for ^{1}H and at 75 MHz for ^{13}C. Deuterated chloroform ($CDCl_3$) was used as the solvent to solubilize the samples, and tetramethylsilane (TMS) was used as an internal standard.

Fourier Transform Infrared Spectroscopy (FTIR). The FTIR spectra were obtained on a PerkinElmer spectrometer model FTIR/NIR FRONTIER, using an attenuated total reflectance (ATR) accessory with zinc selenide (ZnSe) crystal surface, and resolution of 4 cm^{-1} using the arithmetic average of four scans in the wavenumber range of 4000−650 cm^{-1}.

Differential Scanning Calorimetry (DSC). The DSC analyses were performed on a Mettler-Toledo DSC 823e, under N_2 atmosphere (flow rate of 50 mL/min). For the characterization of the monomers, the nonisothermal measurements were performed with a heating rate of 10 °C/min, in a temperature range of 30−400 °C, using approximately 5 mg of samples. All the analyses were performed using aluminum crucibles.

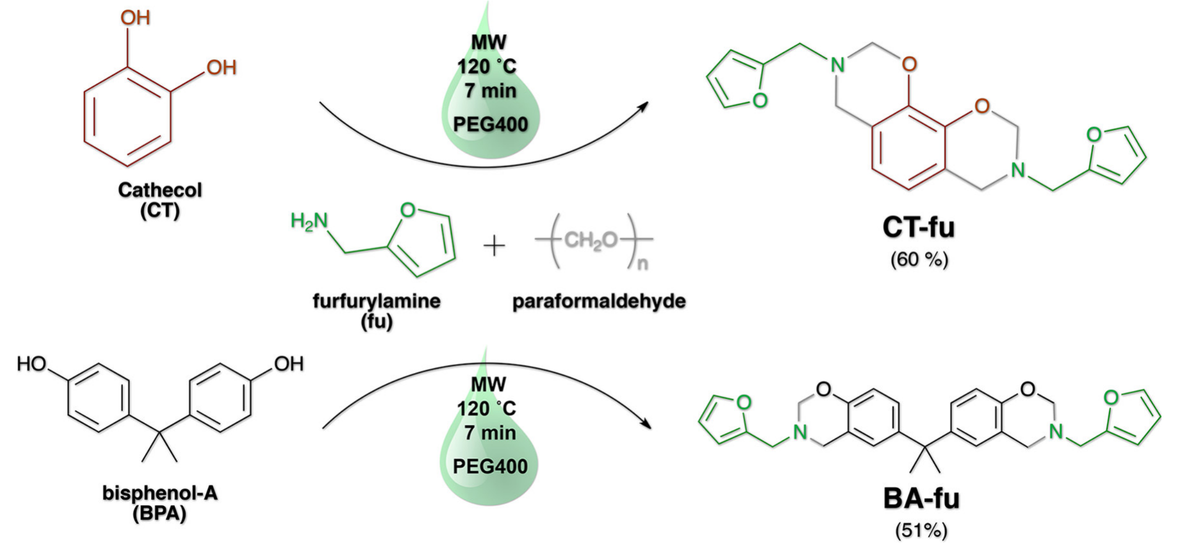
Thermogravimetric analysis (TGA). TGA analyses were performed on a Mettler-Toledo TGA/SDTA 851e, conducted under N_2 atmosphere (flow rate of 50 mL/min) with a heating rate of 10 °C/min in a temperature range of 30 °C to 800 °C. Alumina crucibles were used with approximately 5 mg of samples.

Dynamic Mechanical Analysis (DMA). DMA were conducted on Mettler-Toledo DMA-1, using a single cantilever mode, at a heating rate of 5 °C min^{-1} from 30 °C to 300 °C, using a frequency of 1 Hz in air. The deformation was within the linear viscoelastic limit, determined by a strain sweep test.

Microwave-Assisted Organic Syntheses (MAOS). The microwave-assisted organic syntheses (MAOS) were performed in a Milestone microwave reactor, model StartSYNTH, operating in an open-vessel configuration at a frequency of 2.45 GHz. The temperature set was controlled by a contact-less infrared sensor, and the power applied was limited to 850 W.

*3,8-Bis(furan-2-ylmethyl)-2,3,4,7,8,9-hexahydrobenzo[1,2-e:4,3-e′]bis([1,3]oxazine) (**CT-fu**).* To a 50 mL round-bottom flask equipped with a stirring bar was added PEG-400 (25 mL), catechol (5.00 g, 45.86 mmol), furfurylamine (8.58 mL, 91.75 mmol) and paraformaldehyde (7.24 g, 229.37 mmol). The flask was placed in a microwave cavity and fitted with a Vigreux column. Microwave was set to a maximum power of 850 W, temperature was programmed to increase from room temperature to 120 °C in a period of 2 min; and kept at this temperature for additional 5 min, totaling 7 min under microwave

Scheme 1. Synthetic Scheme for Bis-Benzoxazines CT-fu and BA-fu



irradiation. After the completion of the reaction, the mixture was cooled to room temperature forming a bulky solid phase. This mixture was washed with methanol (4 × 75 mL) and then filtered. After solvent evaporation, 9.22 g (60% yield) of a white powder was obtained and characterized as **CT-fu**.

^{1}H NMR (300 MHz, $CDCl_3$, δ ppm): 7.42 (d, J = 2 Hz, 1H, Ar H), 6.51 (s, 1H, Ar H), 6.34 (m, 1H, Ar H), 6.27 (m, 1H, Ar H), 4.99 (s, 2H, $O-CH_2-N$), 4.00 (s, 2H, $N-CH_2-Fu$), 3.97 (s, 2H, $N-CH_2-Ar$); ^{13}C NMR (75 MHz, $CDCl_3$, δ ppm): 151.8, 142.7, 119.0, 118.7, 110.4, 109.1, 82.7 ($O-CH_2-N$), 49.3 ($Ar-CH_2-N$), 48.6; FT-IR (ATR-ZnSe, cm^{-1}): 1577 (stretching of furan ring), 1478 (stretching of tetrasubstituted benzene ring), 1235 ($C-O-C$ asymmetric stretching), 923 (benzoxazine related mode). Elemental Analysis: C (68.17%), H (5.72%), N (7.95%) (calculated); C (67.53%), H (5.99%), N (7.80%) (found). Molecular weight: 352.38 g·mol^{-1}

*6,6′-(Propane-2,2-diyl)bis(3-(furan-2-ylmethyl)-3,4-dihydro-2H-benzo[e][1,3]oxazine) (**BA-fu**).* The method used to synthesize **BA-fu** was an improved method of Liu and co-workers which used conventional heating.[43] To a 25 mL round-bottom flask equipped with a stirring bar was added PEG-400 (10 mL), bisphenol A (2.00 g, 8.50 mmol), furfurylamine (1.53 mL, 17.00 mmol), and paraformaldehyde (1.34 g, 42.50 mmol). The flask was placed in a microwave cavity and fitted with a Vigreux column. Microwave was set to a maximum power of 850 W, temperature was programmed to increase from room temperature to 120 °C in a period of 2 min; and kept at this temperature for additional 5 min, totaling 7 min under microwave irradiation. After the completion of the reaction, the mixture was cooled to room temperature and then diluted in 100 mL of ethyl acetate. The organic phase was treated with aqueous solution of sodium hydroxide 2 mol L^{-1} (3 × 50 mL) and then with distilled water (3 × 50 mL). The organic phase was dried over sodium sulfate, filtered, and concentrated under reduced pressure to give a yellowish viscous resin. This material was recrystallized with 85 mL of a solvent mixture (hexane:ethyl acetate, 20:1), affording 2.03 g (51% yield) of white crystals characterized as **BA-fu**.

^{1}H NMR (300 MHz, $CDCl_3$, δ ppm): 7.42 (m, 1H; Ar H), 6.99 (dd, J = 9 Hz, J = 3 Hz, 1H, Ar H), 6.83 (d, J = 3 Hz, 1H, Ar H), 6.73 (d, J = 9 Hz), 6.35 (m, 1H, Ar H), 6.26 (m, 1H, Ar H), 4.86 (s, 2H, $O-CH_2-N$), 4.00 (s, 2H, $N-CH_2-Fu$), 3.95 (s, 2H, $N-CH_2-Ar$), 1.62 (s, 3H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$, δ ppm): 151.9, 143.4, 142.7, 126.5, 125.7, 119.0, 116.1, 110.4, 109.0, 81.9 ($O-CH_2-N$), 50.2 ($Ar-CH_2-N$), 48.5, 42.0, 31.3; FTIR (ATR-ZnSe, cm^{-1}), cm^{-1}: 1577 (stretching of furan ring), 1495 (stretching of trisubstituted benzene ring), 1230 ($C-O-C$ asymmetric stretching), 928 (benzoxazine related mode). Elemental Analysis: C (74.02%), H (6.43%), (5.95%) (calculated); C (73.66%), H (6.29%), N (5.87%) (found). Molecular weight: 470.56 g·mol^{-1}

Preparation and (co)polymerization of the Bis-benzoxazines. Three resins were produced containing different amounts of **CT-fu** and **BA-fu**: **CT/BA10** (10% **CT-fu** and 90% **BA-fu**), **CT/BA30** (30% **CT-fu** and 70% **BA-fu**), **CT/BA50** (50% **CT-fu** and 50% **BA-fu**). For the (co)polymerization of the biobased resins, each sample was added to silicone molds (40 × 20 × 2 mm) and then melted and polymerized. The obtained polymers were produced using the following heating schedule: 120 °C (1 h), 140 °C (1 h), 160 °C (1 h), 180 °C (1 h), and 200 °C (2h). The obtained polybenzoxazines were removed from the mold and then put to be post curing at 220 °C (2 h) and 240 °C (2 h).

RESULTS AND DISCUSSION

Design of Sustainable Development of Biobased Bis-Benzoxazines. The bis-benzoxazines were obtained by using a one-pot synthesis of catechol (or BPA), furfurylamine, and paraformaldehyde as shown in Scheme 1. As is frequently observed and reported for the synthesis of bis-benzoxazines, these reactants produced a viscous reaction media, making it very difficult to be homogenized by stirring, and therefore, as an eco-friendly solution for the traditional solvents, a small amount of PEG400 was used.

In many cases, bis-benzoxazine syntheses are performed in the presence of organic solvents in order to keep the reaction media homogeneous since, depending on the compounds involved, high viscosity and/or low miscibility could prevent the maintenance of local stoichiometry and successful occurrence of reaction. Therefore, utilization of a solvent is needed.[6]

In this work, PEG was not only successfully employed as an alternative nontoxic solvent, but its unique properties allowed us to (i) promptly synthesize a fully biobased bis-benzoxazine in only 7 min under microwave irradiation; and (ii) to easily isolate the product by simply filtering and washing with small portions of methanol, which was completely recycled through rotatory evaporation by the end of purification procedure.

The intermolecular forces that predominate between PEG molecules are of hydrogen bonds and dipole−dipole types. These kinds of forces promote better interactions among polar, or relatively polar, substances—as catechol (**CT**), furfurylamine (**fu**) and formaldehyde—but are unable to effectively interact

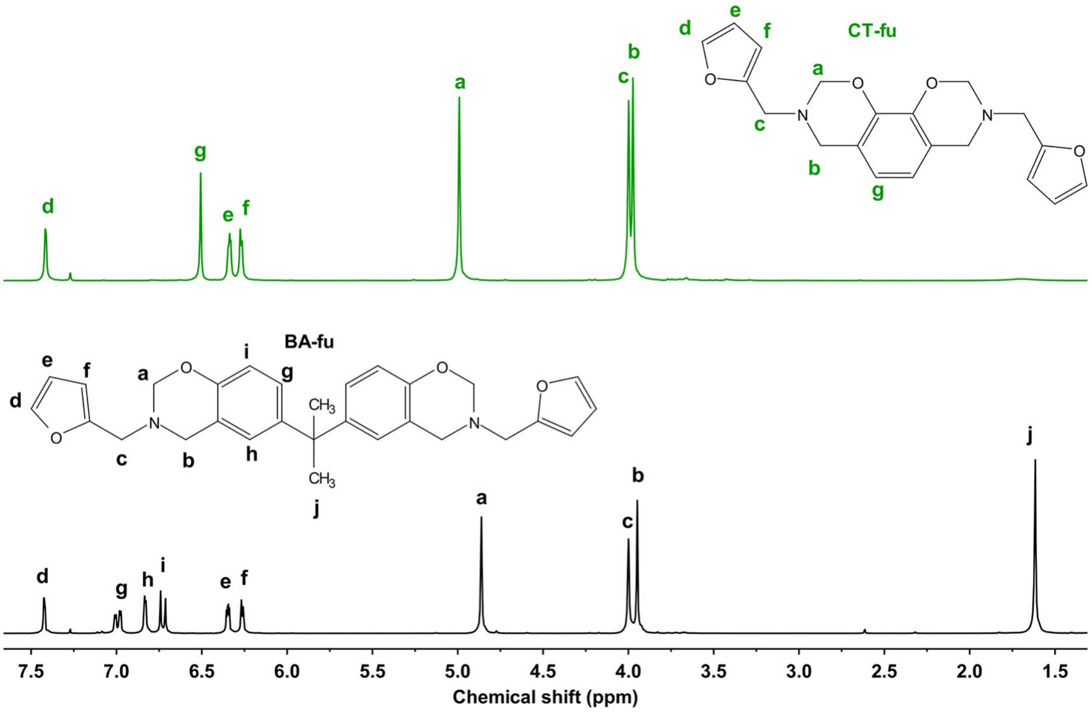


Figure 1. ^{1}H NMR spectra of **CT-fu** and **BA-fu**.

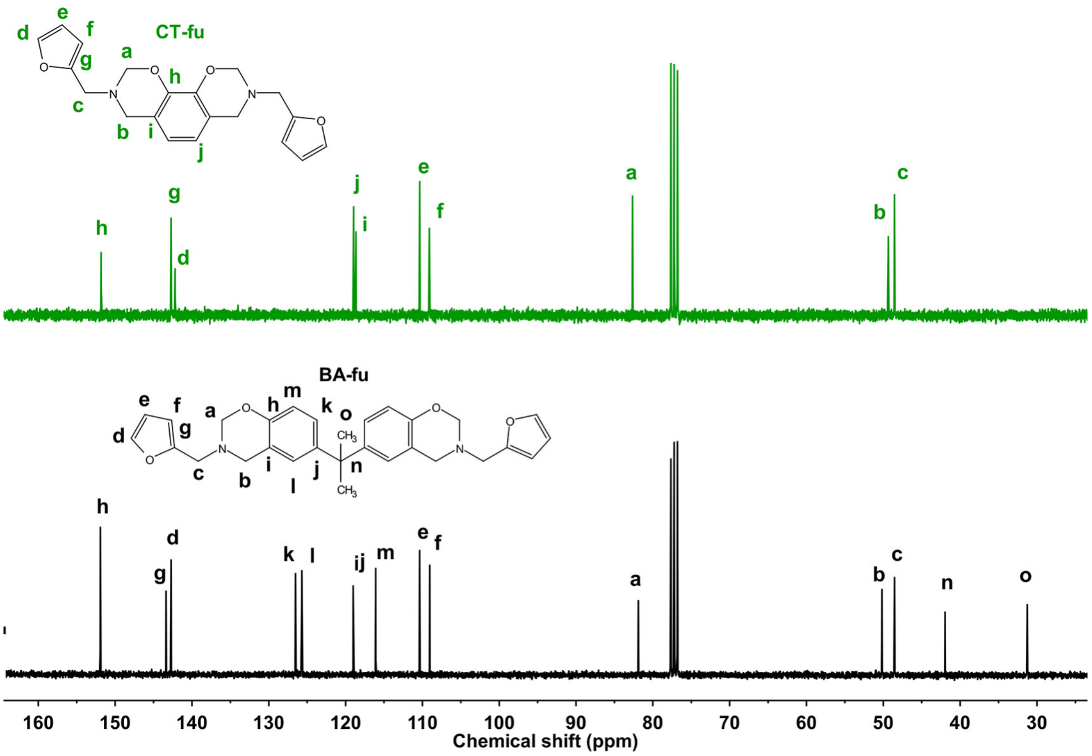


Figure 2. ^{13}C NMR spectra of **CT-fu** and **BA-fu**.

with nonpolar compounds, which is the case of the desired product (**CT-fu**), in which intermolecular interactions are basically driven by π-stacking, promoting the formation of more compact and rigid structure.[40] Due to these properties, solvent cooling and simple addition of small amounts of methanol was sufficient for the complete precipitation of the product.

Due also to its high capacity to convert MW radiation into heat, PEG proved to be an outstanding reaction media for microwave-assisted organic synthesis, reducing drastically the reaction time and the amount of energy required to promoting its efficient heating. The likelihood of the ring closure of an open Mannich base into oxazine ring depends on the dielectric constant of the solvent, being smaller the dielectric constant the higher the probability of ring closure. The dielectric constant of PEG is approximately 8−12, and thus it does not interfere significantly the ring closure reaction.[41]

Bis-benzoxazines can be synthesized under microwave irradiation[42] and, more recently, our group reported a systematic study on the microwave-assisted synthesis of monofunctional benzoxazines under solvent-free conditions,[43] from which the actual parameters reported here were based.

To validate and expand the applicability of the procedure described, we also reproduced these conditions using BPA as the phenolic moiety instead of catechol (Scheme 1). The method proved to be very effective also for the synthesis of the partially biobased bis-benzoxazine **BA-fu**. It further points to a possibility that the approach described in the current paper might be universally applicable to many other benzoxazines. When compared to a previously reported synthetic methodology,[44] which used dioxane as solvent and traditional heating for 24 h, the procedure described here provided the same product in similar yields, but with dramatic reduction of time and under eco-friendly conditions.

Under these circumstances, both the product and process described in this work proved to be very effective and highly eco-friendly, as featured by (a) the use PEG as an innocuous and inexpensive solvent; (b) of microwave irradiation as heating source; (c) much shorter reaction times; (d) no use of catalyst or auxiliary reactants; and (e) good yields. These aspects are properly inserted within the green chemistry principles, which emphasize, among others, the use of renewable feedstock, safer solvents, energy efficiency and atom economy.[18]

Structural Characterization of Bis-Benzoxazines. The molecular structures of the monomers were confirmed by ^{1}H (Figure 1) and ^{13}C NMR (Figure 2) and by FTIR. It was noticed that the chemical shifts of the oxazinic methylenes were very similar by analyzing the ^{1}H and the ^{13}C NMR spectra. In the ^{1}H NMR spectra the structures of the obtained products were confirmed by the presence of the two singlets in the regions of 5.10 to 4.80 ppm and 3.98 to 3.93 ppm, which represents the two methylenes of the oxazinic group. The chemical structure of **CT-fu** was compared with the **H-fu** and **R-fu** of Dumas and co-workers,[10] and it was shown that **CT-fu** did not have any isomer or oligomers such as of **H-fu** and **R-fu**.

The presence of the oxazinic methylenes was also confirmed by ^{13}C NMR spectra with the peaks at around 82 and 50 ppm.

One of the concerns about this synthetic procedure was that side-products could be formed after a possible nucleophilic attack from the terminal hydroxyl groups of PEG to the oxazine ring. But, recently, Brown and Rider[33] described the utilization of poly(ethylene glycol) as a grafting agent for the synthesis of low T_g polybenzoxazines and no interaction from PEG's hydroxyl end-group to the oxazine was observed.

As the NMR spectra demonstrate, PEG was not incorporated in the monomer, indicating its low reactivity in the reported conditions and, therefore, can be efficiently used as solvent.

In Figure 3 are shown the FTIR spectra of **CT-fu** and **BA-fu** and their respective polymers, **poly(CT-fu)** and **poly(BA-fu)**, which were necessary for a better understanding of the vibrational modes of the bis-benzoxazines and their polybenzoxazines.

The absence of the bands from the region between 3100 to 3600 cm^{-1} confirms that the hydroxyl groups are not present on the monomers, suggesting the transformation into bis-oxazine rather than mono-oxazine structure. The band at 1479 cm^{-1} is attributed to tetrasubstituted benzene ring of **CT-fu**, and the band at 1495 cm^{-1} is attributed to the trisubstituted benzene ring of **BA-fu**. The presence of the oxazine ring was observed by the C−O−C asymmetric stretching modes of the bands at 1235 cm^{-1} for **CT-fu** and 1230 cm^{-1} for **BA-fu,** and also by the benzoxazine related mode[45] at 923 and 928 cm^{-1} for **CT-fu** and **BA-fu**, respectively. The presence of the furan ring in the structure of **CT-fu** and **BA-fu** was confirmed by the appearance of bands at 1578 and 1585 cm^{-1}, respectively.[44] Also in the FTIR spectra, the absence of a broad and intense band at 1094 cm^{-1} indicates no insertion of PEG in the molecular structures of the products.

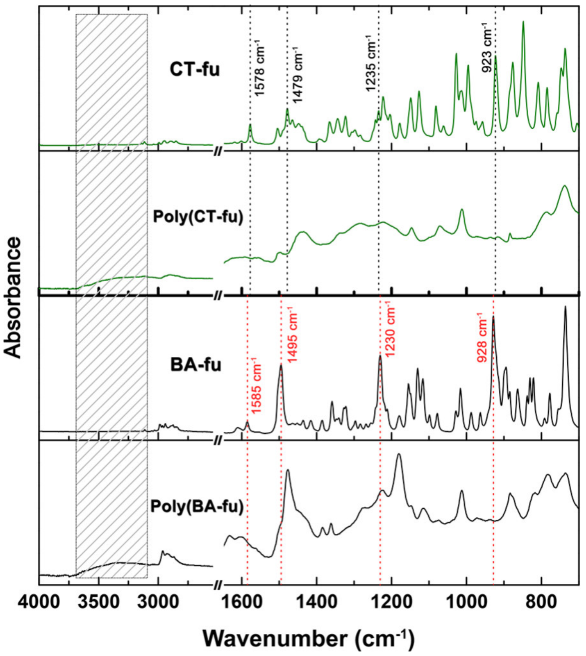


Figure 3. FTIR spectra of **CT-fu** and **BA-fu**.

After polymerization of the monomers, it was observed the disappearance of the bands regarding the C−O−C asymmetric stretching (around 1230 cm^{-1}) and the benzoxazine related modes (around 920 cm^{-1}), confirming the successful cleavage of the oxazine ring. After the ring-opening process of **CT-fu**, it was also observed that the electrophilic substitution occurred on the substituted benzene rings of the benzoxazines, as their respective bands disappeared, while for **BA-fu** the respective bands was displaced to lower wavenumbers. Another observation made was the broad absorption around 1610 cm^{-1}, which indicate that electrophilic substitutions occurred also on the furfuryl groups.[44]

Polymerization Behavior of the Bis-Benzoxazines. The thermal behavior of the bis-benzoxazines monomers was monitored by DSC (Figure 4). The obtained data are summarized in Table 1.

It was observed that the endothermic events, which represent the melting points (T_m), of the two bis-benzoxazines were quite distinct. The mp of **CT-fu** was higher than that of **BA-fu**, which was expected since both oxazine rings of **CT-fu** are fused to the same benzene, making it a much more rigid and compact molecule when compared to **BA-fu**, where the oxazine rings are separated by an alkyl bridge, which gives flexibility to this structure.

The exothermic events, corresponding to the temperature range of the ring-opening polymerization (ROP) of the monomers, demonstrated also different behaviors. While the **BA-fu** monomer exhibits a broad exothermic event between 220 and 300 °C, with an initial polymerization temperature

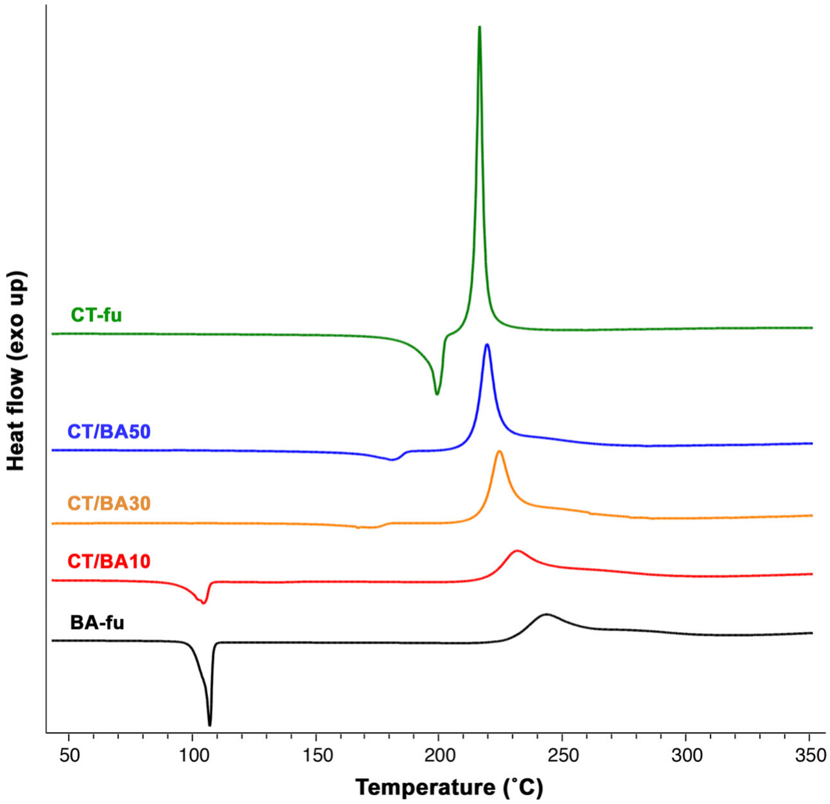


Figure 4. DSC curves of **CT-fu**, **BA-fu**, and different resins compositions (**CT-fu**/**BA-fu**).

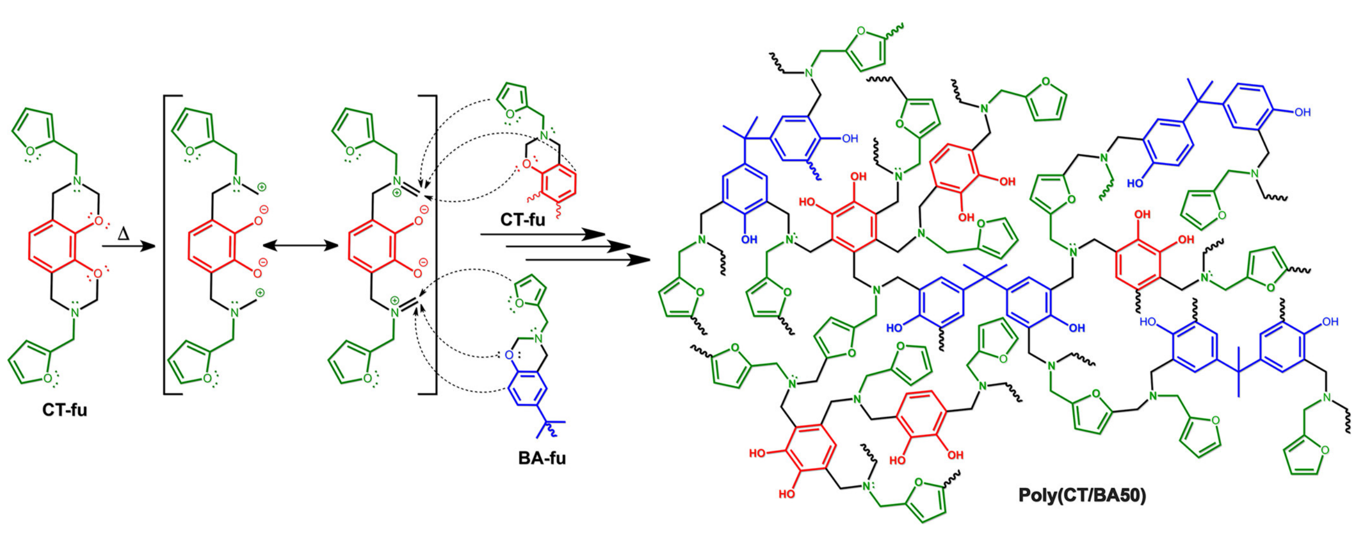
Table 1. Data of DSC Curves of CT-fu, BA-fu and Different Resins Compositions (CT-fu/BA-fu)

sample	T_m (°C)	T_0 (°C)	T_p (°C)	ΔH (J g^{-1})	ΔH (kJ mol^{-1})
CT-fu	198	213	220	381	134.1
BA-fu	105	223	240	246	115.6
CT/BA10	104	220	232	251	
CT/BA30	167	216	225	331	
CT/BA50	181	214	221	346	

(T_0) at 223 °C, the **CT-fu** monomer has a sharp exothermic event between 205 and 240 °C, with T_0 at 213 °C. It was also observed that the enthalpy of polymerization value (ΔH) of **CT-fu** is more than 50% greater than that obtained for **BA-fu**. The obtained results for **BA-fu** are consistent with those reported by Liu and Chou.[44]

Due to the proximity of the fusion and polymerization events (processing window) of **CT-fu**, it becomes very difficult to process the monomer in order to obtain an intact and defects-free polymer. A strategy to solve this problem is by polymerizing the monomer under high pressure[46] or by copolymerizing this monomer with another one that possesses a lower melting point. Thus, it was proposed to blend the two bis-benzoxazines in different concentrations, which could lead

Scheme 2. Representative Copolymerization Mechanism CT-fu and BA-fu



to resins with better processing windows, and therefore to high quality polybenzoxazines samples, liable to have their mechanical properties analyzed by DMA.

For this, three different resin compositions were prepared, as described in the Experimental Section, namely: **CT/BA10**, **CT/BA30**, and **CT/BA50.**

Analyzing the DSC thermograms of the monomer mixtures (Figure 4), it was noticed only one endothermic event, indicating that the monomers are well compatible to be fused simultaneously.

It was also observed that with the increased content of **CT-fu**, the polymerization peak temperature (T_p) was decreased, while the extrapolated onset polymerization temperature (T_0) was practically maintained. This demonstrates that the polymerization initiates with the oxazine ring-opening of **CT-fu**, catalyzing the polymerization process of **BA-fu**, as depicted in Scheme 2. These polymerization behaviors of the resins were expected since **CT-fu** has a lower polymerization temperature than **BA-fu**.

Thermal Analysis of the Biobased Polybenzoxazines. The thermal stability of polybenzoxazines was evaluated by thermogravimetric analysis (TGA) under inert atmosphere (N_2). The TGA thermograms of **poly(BA-fu)**, **poly(CT/BA10)**, **poly(CT/BA30)**, and **poly(CT/BA50)** are shown in Figure 5 and their data summarized in Table 2. Analyzing the extrapolated onset degradation temperature (T_0) it was noticed that **poly(BA-fu)** present a higher initial degradation than its copolymers with **CT-fu**. Nevertheless, as the **CT-fu** content increased, the char yields (CY) values of the copolymers were also increased. The copolymer with the highest biobased content, **poly(CT/BA50)**, had a 14% increase in char yield when compared with **poly(BA-fu)**.

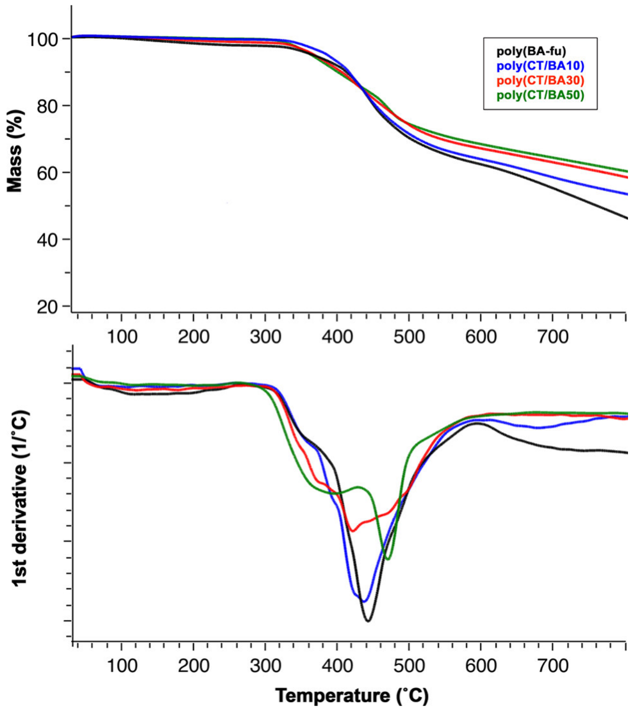


Figure 5. TGA curves of poly(BA-fu), poly(CT/BA10), poly(CT/BA30), and poly(CT/BA50).

Compared to results previously published for the classical bisphenol A/aniline (**BA-a or P-BPA-ABz**) based polybenzoxazine,[7,47−49] the polybenzoxazines reported in this work presented superior thermal stability. With the incremental incorporation of **CT-fu** into **BA-fu**, not only the biomass-derived content was increased (up to 50% w/w), but, especially, the generation of carbonaceous residue (CY).

Considering the elevated values of char yield observed, TGA results were also employed to evaluate the flame retardancy of the polybenzoxazines by the determination of the limiting oxidation index (LOI), which is the minimum O_2 concentration to let the material ignite to cause flammability. Materials with LOI values ≤26 are considered flammable and an interesting way to estimate LOI values of halogen-free polymers is by using the char yields of TGA analyses using the van Krevelen equation (eq 1).[50]

$$\mathrm{LOI} = 17.5 + 0.4(\mathrm{CY}) \tag{1}$$

The correlation of LOI values and CY has been used extensively,[51−56] and this method is convenient when the amount of the available samples are highly limited. The LOI values of these polybenzoxazines indicate that these halogen-, silane-, and phosphorus-free materials possesses outstanding flame retardancy, as polymers containing LOI values >28 are considered as self-extinguishing.[52] The flame retardancy of these polybenzoxazines was shown to be superior to the polybenzoxazine of the commercially available **BA-a**, which possesses a LOI value of 30.3.[57] and also superior than polyepoxy of the commercially available DGEBA epoxy resin, with LOI values around 20.5 to 24.6.[58−60]

The mechanical properties of the polybenzoxazines were evaluated by DMA to assess the effect of the different compositions of benzoxazine monomers (**CT-fu** and **BA-fu**) in dynamic mechanical properties against temperature. The DMA curves of the storage modulus (E') and the damping factor (tan δ) as a function of temperature of the polybenzoxazines are shown in Figure 6, and their data are summarized in Table 3.

The use of **CT-fu** as a comonomer demonstrated a significant improvement on the storage modulus of the polybenzoxazines, starting from 2.4 GPa of **poly(BA-fu)** to 3.5 GPa of **poly(CT/BA50)** at 30 °C. Along the entire glassy state, the copolymers also demonstrated superior storage modulus than the homopolymer. At 300 °C the storage modulus of **poly(BA-fu)** and **poly(CT/BA10)** demonstrated to be higher than 1 GPa, indicating that these materials

Table 2. Data of TGA Curves of Poly(BA-fu), Poly(10%), Poly(30%), and Poly(50%)

name	T_0 (°C)	T_5 (°C)	T_{10} (°C)	T_{20} (°C)	CY (%)	LOI[a]
poly(BA-fu)	338	361	410	444	46	35.9
poly(CT/BA10)	336	384	414	443	53	38.7
poly(CT/BA30)	331	365	403	446	58	40.7
poly(CT/BA50)	329	361	397	458	60	41.5

[a] Calculated from the char yield at 800 °C of TGA analysis.

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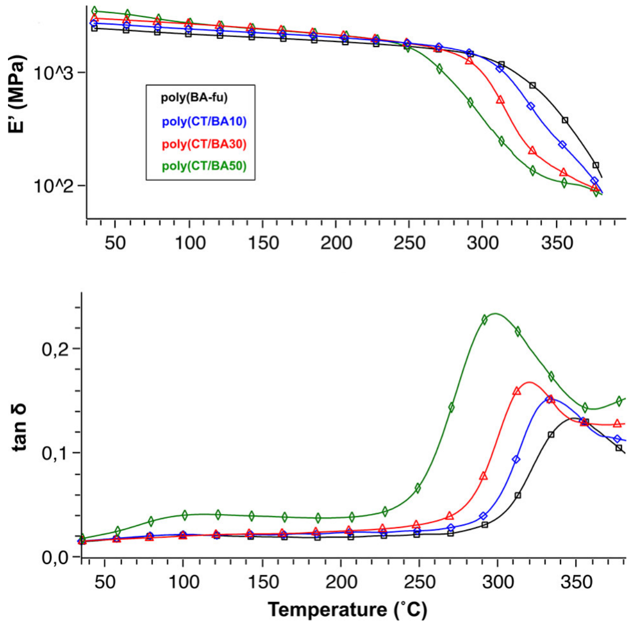

Figure 6. DMA curves of poly(BA-fu), poly(CT/BA10), poly(CT/BA30), and poly(CT/BA50).

possesses reasonably high cross-link density.[6] However, by analyzing the E' at the same temperature of the other polybenzoxazines, it was noticed that the cross-link densities of the copolymers tended to be lower as the **CT-fu** content increased.

Reduction in the glass transition temperature (T_g), determined as the temperature at the tan δ peak, was observed as CT-fu content increased. Somehow, the incorporation of CT-fu into the polymeric matrix disrupted the polymer network, changing the molecular structure and increasing the mobility of polymer chains, impairing the mechanical properties.

From the DMA results, it is also possible to correlate T_g and E' with the **CT-fu** concentration, as plotted in Figure 7. This observation could indicate a good reliability on the homogeneous distributions of the **CT-fu/BA-fu** units in the polymer matrices, suggesting a good processability and compatibility of the monomer mixtures. The height of tan δ peak can be interpreted as the extent of mobility of the polymeric segments at a determined temperature.[61] As observed in Figure 6, increased amounts of **CT-fu** caused an increase in the tan δ peak, indicating higher energy loss and a more viscous behavior.[55] All the copolymers showed higher tan δ peak heights than that of the homopolymer. Since an increase in cross-link density typically results in an enhancement of the mechanical properties with the restricted mobility of the polymeric matrix, it was expected that the increase of **CT-fu** content could provide higher cross-link densities on the copolymers, since more reactive furfuryl moieties (mols per mass of monomers) would be available.[8] However, further investigation is required to a better understand why the increase of **CT-fu** units in the polymer increases significantly the E' of the polybenzoxazines at lower temperatures but impairs the thermomechanical stability of the polymers at higher temperatures.

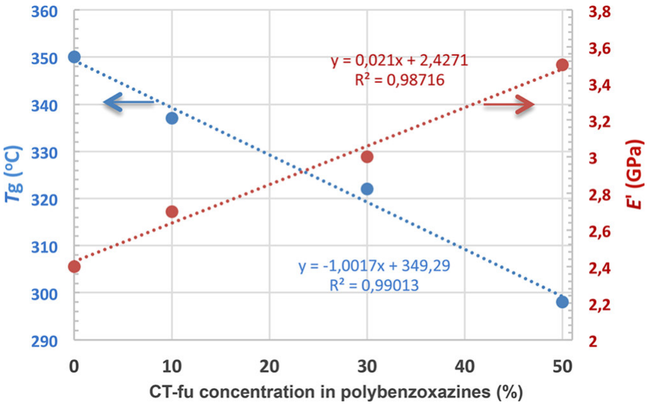

Figure 7. Linear correlations of T_g and E' with **CT-fu** concentrations.

Nevertheless, these (co)polymers are very promising as high-performance materials due to their elevated thermal stabilities, high storage moduli, and high T_g, which can reach temperatures up to 300 °C.

■ CONCLUSIONS

The results presented here suggest that the synthesis of a fully biobased benzoxazine starting from the lignocellulose-derived products, catechol and furfurylamine, is a valuable tool for the sustainable development of bis-benzoxazine resins. Microwave irradiation along with poly(ethylene glycol) allowed the successful synthesis of thermosetting resins in a matter of few minutes and without the use of toxic chemicals in good yields. Nevertheless, further investigation is being carried out looking forward to the production of benzoxazine resins in larger scales and the effective reuse of PEG. The incorporation of **CT-fu** into **BA-fu** produced high-performance polybenzoxazines with elevated biobased contents. This novel fully biobased monomer was also responsible for the incredible LOI value presented by **poly(CT/BA50)**, replacing 50% (w/w) of **BA-fu** and giving a copolymer with attractive flame retardant properties.

In this work, we also attempted to demonstrate that lignocellulosic biomass represents a valuable renewable feedstock for the development of highly biobased derived benzoxazine resins, which can be turned into high-performance thermoset materials.

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Table 3. Data of DMA Curves of Poly(BA-fu), Poly(CT/BA10), Poly(CT/BA30), and Poly(CT/BA50)

sample	E' at 30 °C (GPa)	E' at 200 °C (GPa)	E' at 300 °C (GPa)	T_g (°C)	tan δ height
poly(BA-fu)	2.4	1.8	1.3	350	0.13
poly(CT/BA10)	2.7	2.0	1.3	337	0.15
poly(CT/BA30)	3.0	2.1	1.0	322	0.16
poly(CT/BA50)	3.5	2.1	0.4	298	0.23

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) Raquez, J.-M.; Deléglise, M.; Lacrampe, M.-F.; Krawczak, P. Thermosetting (bio)materials derived from renewable resources: A critical review. *Prog. Polym. Sci.*. **2010**, *35* (4), 48710.1016/j.progpolymsci.2010.01.001.

(2) Ishida, H.; Agag, T. Handbook of Benzoxazine Resins. In *Handbook of Benzoxazine Resins*; Ishida, H., Agag, T., Eds.; Elsevier: Oxford, 2011; Chapter 1.

(3) Froimowicz, P.; Zhang, K.; Ishida, H. Intramolecular Hydrogen Bonding in Benzoxazines: When Structural Design Becomes Functional. *Chem.—Eur. J.*. **2016**, *22* (8), 269110.1002/chem.201503477.

(4) Takeichi, T.; Kawauchi, T.; Agag, T. High Performance Polybenzoxazines as a Novel Type of Phenolic Resin. *Polym. J.*. **2008**, *40* (12), 112110.1295/polymj.PJ2008072.

(5) Kiskan, B.; Ghosh, N. N.; Yagci, Y. Polybenzoxazine-based composites as high-performance materials. *Polym. Int.*. **2011**, *60* (2), 16710.1002/pi.2961.

(6) Lin, C. H.; Chen, Z. J.; Chen, C. H.; Wang, M. W.; Juang, T. Y. Synthesis of a Bisbenzylideneacetone-Containing Benzoxazine and Its Photo- and Thermally Cured Thermoset. *ACS Omega* **2017**, *2* (7), 343210.1021/acsomega.7b00573.

(7) Hassan, W. A. W.; Liu, J.; Howlin, B. J.; Ishida, H.; Hamerton, I. Examining the influence of bisphenol A on the polymerisation and network properties of an aromatic benzoxazine. *Polymer* **2016**, *88*, 5210.1016/j.polymer.2016.01.041.

(8) Froimowicz, P.; Arza, C. R.; Han, L.; Ishida, H. Smart, Sustainable, and Ecofriendly Chemical Design of Fully Bio-Based Thermally Stable Thermosets Based on Benzoxazine Chemistry. *ChemSusChem* **2016**, *9* (15), 192110.1002/cssc.201600577.

(9) Wang, C.-F.; Wang, Y.-T.; Tung, P.-H.; Kuo, S.-W.; Lin, C.-H.; Sheen, Y.-C.; Chang, F.-C. Stable Superhydrophobic Polybenzoxazine Surfaces over a Wide pH Range. *Langmuir* **2006**, *22* (20), 828910.1021/la061480w.

(10) Dumas, L.; Bonnaud, L.; Olivier, M.; Poorteman, M.; Dubois, P. High performance bio-based benzoxazine networks from resorcinol and hydroquinone. *Eur. Polym. J.*. **2016**, *75*, 48610.1016/j.eurpolymj.2016.01.021.

(11) Sini, N. K.; Azechi, M.; Endo, T. Synthesis and Properties of Spiro-Centered Benzoxazines. *Macromolecules* **2015**, *48* (20), 746610.1021/acs.macromol.5b01970.

(12) Zhang, L.; Yang, Y.; Chen, Y.; Lu, H. Cardanol-capped main-chain benzoxazine oligomers for resin transfer molding. *Eur. Polym. J.*. **2017**, *93*, 28410.1016/j.eurpolymj.2017.06.006.

(13) Li, W.; Wei, T.; Gao, Y.; Xi, K.; Jia, X. Preparation of novel benzoxazine monomers containing ferrocene moiety and properties of polybenzoxazines. *Polymer* **2012**, *53* (6), 123610.1016/j.polymer.2012.01.052.

(14) Wang, C.-F.; Su, Y.-C.; Kuo, S.-W.; Huang, C.-F.; Sheen, Y.-C.; Chang, F.-C. Low-surface-free-energy materials based on polybenzoxazines. *Angew. Chem., Int. Ed.*. **2006**, *45* (14), 224810.1002/anie.200503957.

(15) Trita, A. S.; Over, L. C.; Pollini, J.; Baader, S.; Riegsinger, S.; Meier, M. A. R.; Gooßen, L. J. Synthesis of potential bisphenol A substitutes by isomerising metathesis of renewable raw materials. *Green Chem.*. **2017**, *19* (13), 305110.1039/C7GC00553A.

(16) Gramec Skledar, D.; Peterlin Mašič, L. Bisphenol A and its analogs: Do their metabolites have endocrine activity? *Environ. Toxicol. Pharmacol.*. **2016**, *47*, 18210.1016/j.etap.2016.09.014.

(17) Chiu, W.-M.; Wang, Y.-X.; Tsai, P.-A.; Wu, J.-H. Preparation and characterization of novel polybenzoxazine hybrid materials. *High Perform. Polym.*. **2016**, *28* (8), 97110.1177/0954008315612139.

(18) Anastas, P. T.; Warner, J. C. *Green Chemistry: Theory and Practice*; Oxford University Press: New York, 1998.

(19) Lligadas, G.; Tüzün, A.; Ronda, J. C.; Galià, M.; Cádiz, V. Polybenzoxazines: new players in the bio-based polymer arena. *Polym. Chem.*. **2014**, *5* (23), 663610.1039/C4PY00914B.

(20) Ambrožič, R.; Šebenik, U.; Krajnc, M. Synthesis, curing kinetics, thermal and mechanical behavior of novel cardanol-based benzoxazines. *Polymer* **2015**, *76*, 20310.1016/j.polymer.2015.08.065.

(21) Teong, S. P.; Yi, G.; Zhang, Y. Hydroxymethylfurfural production from bioresources: past, present and future. *Green Chem.*. **2014**, *16* (4), 201510.1039/c3gc42018c.

(22) Kotzebue, L. R. V.; Ribeiro, F. W. M.; Sombra, V. G.; Feitosa, J. P. A.; Mele, G.; Mazzetto, S. E.; Lomonaco, D. Spectral and thermal studies on the synthesis and catalyzed oligomerization of novel cardanol-based benzoxazines. *Polymer* **2016**, *92*, 18910.1016/j.polymer.2016.04.005.

(23) Calò, E.; Maffezzoli, A.; Mele, G.; Martina, F.; Mazzetto, S. E.; Tarzia, A.; Stifani, C. Synthesis of a novel cardanol-based benzoxazine monomer and environmentally sustainable production of polymers and bio-composites. *Green Chem.*. **2007**, *9* (7), 75410.1039/b617180j.

(24) Attanasi, O. A.; Behalo, M. S.; Favi, G.; Lomonaco, D.; Mazzetto, S. E.; Mele, G.; Pio, I.; Vasapollo, G. Solvent Free Synthesis of Novel Mono- and Bis-Benzoxazines from Cashew Nut Shell Liquid Components. *Curr. Org. Chem.*. **2012**, *16* (21), 261310.2174/138527212804004616.

(25) Xu, H.; Zhang, W.; Lu, Z.; Zhang, G. Hybrid polybenzoxazine with tunable properties. *RSC Adv.*. **2013**, *3* (11), 367710.1039/c3ra22247k.

(26) Sini, N. K.; Bijwe, J.; Varma, I. K. Renewable benzoxazine monomer from Vanillin: Synthesis, characterization, and studies on curing behavior. *J. Polym. Sci., Part A: Polym. Chem.*. **2014**, *52* (1), 710.1002/pola.26981.

(27) Phalak, G. A.; Patil, D. M.; Mhaske, S. T. Synthesis and characterization of thermally curable guaiacol based poly(benzoxazine-urethane) coating for corrosion protection on mild steel. *Eur. Polym. J.*. **2017**, *88*, 9310.1016/j.eurpolymj.2016.12.030.

(28) Dumas, L.; Bonnaud, L.; Olivier, M.; Poorteman, M.; Dubois, P. Eugenol-based benzoxazine: from straight synthesis to taming of the network properties. *J. Mater. Chem. A* **2015**, *3* (11), 601210.1039/C4TA06636G.

(29) Bilal, M.; Asgher, M.; Iqbal, H. M. N.; Hu, H.; Zhang, X. Biotransformation of lignocellulosic materials into value-added products—A review. *Int. J. Biol. Macromol.* **2017**, *98*, 44710.1016/j.ijbiomac.2017.01.133.

(30) Jeenpadiphat, S.; Mongkolpichayarak, I.; Tungasmita, D. N. Catechol production from lignin by Al-doped mesoporous silica catalytic cracking. *J. Anal. Appl. Pyrolysis* **2016**, *121*, 31810.1016/j.jaap.2016.08.011.

(31) Chen, Z.; Wan, C. Biological valorization strategies for converting lignin into fuels and chemicals. *Renewable Sustainable Energy Rev.*. **2017**, *73*, 61010.1016/j.rser.2017.01.166.

(32) Trejo-Machin, A.; Verge, P.; Puchot, L.; Quintana, R. Phloretic acid as an alternative to the phenolation of aliphatic hydroxyls for the elaboration of polybenzoxazine. *Green Chem.*. **2017**, *19* (21), 506510.1039/C7GC02348K.

(33) Brown, E. A.; Rider, D. A. Pegylated Polybenzoxazine Networks with Increased Thermal Stability from Miscible Blends of Tosylated Poly(ethylene glycol) and a Benzoxazine Monomer. *Macromolecules* **2017**, *50* (17), 646810.1021/acs.macromol.7b01457.

(34) Poly(Ethylene Glycol) Chemistry. In *Biotechnical and Biomedical Applications*; Harris, J. M., Ed.; Springer US: Boston, MA, 1992.

(35) Chen, R. J.; Spear, S. K.; Huddleston, J. G.; Rogers, R. D. Polyethylene glycol and solutions of polyethylene glycol as green reaction media. *Green Chem.*. **2005**, *7* (2), 6410.1039/b413546f.

(36) Vafaeezadeh, M.; Hashemi, M. M. Polyethylene glycol (PEG) as a green solvent for carbon-carbon bond formation reactions. *J. Mol. Liq.*. **2015**, *207*, 7310.1016/j.molliq.2015.03.003.

(37) Cini, E.; Petricci, E.; Taddei, M. Pd/C Catalysis under Microwave Dielectric Heating. *Catalysts* **2017**, *7* (3), 8910.3390/catal7030089.

(38) Driowya, M.; Saber, A.; Marzag, H.; Demange, L.; Benhida, R.; Bougrin, K. *Microwave-assisted synthesis of bioactive six-membered heterocycles and their fused analogues*; 2016; Vol. *21*.

(39) Kappe, C. O. Controlled Microwave Heating in Modern Organic. *Angew. Chem., Int. Ed.*. **2004**, *43* (46), 625010.1002/anie.200400655.

(40) Martinez, C. R.; Iverson, B. L. Rethinking the term "pi-stacking. *Chem. Sci.*. **2012**, *3* (7), 219110.1039/c2sc20045g.

(41) Agag, T.; Jin, L.; Ishida, H. A new synthetic approach for difficult benzoxazines: Preparation and polymerization of 4,4′-diaminodiphenyl sulfone-based benzoxazine monomer. *Polymer* **2009**, *50* (25), 594010.1016/j.polymer.2009.06.038.

(42) Manikannan, R.; Muthusubramanian, S. Synthesis and biological activity of 6-alkyl/chloro-3-{4-(6-alkyl/chloro-2H-benzo[e][1,3]-oxazin-3(4H)-yl}-3,4-dihydro-2H-benzo[e][1,3]oxazines. *Indian J. Chem.* **2010**, *49B*, 1083−1087.

(43) Oliveira, J. R.; Kotzebue, L. R. V; Ribeiro, F. W. M.; Mota, B. C.; Zampieri, D.; Mazzetto, S. E.; Ishida, H.; Lomonaco, D. 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., Part A: Polym. Chem.*. **2017**, *55* (21), 353410.1002/pola.28755.

(44) Liu, Y.-L.; Chou, C.-I. High performance benzoxazine monomers and polymers containing furan groups. *J. Polym. Sci., Part A: Polym. Chem.*. **2005**, *43* (21), 526710.1002/pola.21023.

(45) Han, L.; Iguchi, D.; Gil, P.; Heyl, T. R.; Sedwick, V. M.; Arza, C. R.; Ohashi, S.; Lacks, D. J.; Ishida, H. Oxazine Ring-Related Vibrational Modes of Benzoxazine Monomers Using Fully Aromatically Substituted, Deuterated, 15 N Isotope Exchanged, and Oxazine-Ring-Substituted Compounds and Theoretical Calculations. *J. Phys. Chem. A* **2017**, *121* (33), 626910.1021/acs.jpca.7b05249.

(46) Shen, S. B.; Ishida, H. Synthesis and characterization of polyfunctional naphthoxazines and related polymers. *J. Appl. Polym. Sci.*. **1996**, *61* (9), 159510.1002/(SICI)1097-4628(19960829)61:9<1595::AID-APP19>3.0.CO;2-P.

(47) Dayo, A. Q.; Gao, B.-c.; Wang, J.; Liu, W.-b.; Derradji, M.; Shah, A. H.; Babar, A. A. Natural hemp fiber reinforced polybenzoxazine composites: Curing behavior, mechanical and thermal properties. *Compos. Sci. Technol.*. **2017**, *144*, 11410.1016/j.compscitech.2017.03.024.

(48) Kopsidas, S.; Hamerton, I. Examining the thermal behaviour of novel aromatic polybenzoxazine blends containing an organophosphorous compound and polyhedral oligomeric silsesquioxane reagents. *Polym. Int.*. **2016**, *65* (9), 101510.1002/pi.5139.

(49) Douse, E.; Kopsidas, S.; Jesson, D.; Hamerton, I. Modification of stress-strain behaviour in aromatic polybenzoxazines using core shell rubbers. *React. Funct. Polym.*. **2016**, *103*, 11710.1016/j.reactfunctpolym.2016.04.009.

(50) van Krevelen, D. W. Some basic aspects of flame resistance of polymeric materials. *Polymer* **1975**, *16* (8), 61510.1016/0032-3861(75)90157-3.

(51) Deng, C.; Yin, H.; Li, R.-M.; Huang, S.-C.; Schartel, B.; Wang, Y.-Z. Modes of action of a mono-component intumescent flame retardant MAPP in polyethylene-octene elastomer. *Polym. Degrad. Stab.*. **2017**, *138*, 14210.1016/j.polymdegradstab.2017.03.006.

(52) Mallakpour, S.; Zadehnazari, A. Improved covalent functionalization of multi-walled carbon nanotubes using ascorbic acid for poly(amide−imide) composites having dopamine linkages. *Bull. Mater. Sci.*. **2017**, *40* (1), 21310.1007/s12034-017-1358-4.

(53) Thirukumaran, P.; Shakila Parveen, A.; Kumudha, K.; Sarojadevi, M. Synthesis and characterization of new polybenzoxazines from renewable resources for bio-composite applications. *Polym. Compos.*. **2016**, *37* (2), 182110.1002/pc.23356.

(54) Fu, T.; Guo, D.-M.; Wu, J.-N.; Wang, X.-L.; Wang, X.-L.; Chen, L.; Wang, Y.-Z. Inherent flame retardation of semi-aromatic polyesters via binding small-molecule free radicals and charring. *Polym. Chem.*. **2016**, *7* (8), 158410.1039/C5PY01938A.

(55) Kaliavaradhan, K.; Muthusamy, S. Synthesis and characterization of various phenylene diamine-based bismaleimide-containing phthalonitrile resins. *Polym. Bull.*. **2016**, *73* (7), 192110.1007/s00289-015-1585-z.

(56) Dumas, L.; Bonnaud, L.; Olivier, M.; Poorteman, M.; Dubois, P. Chavicol benzoxazine: Ultrahigh Tg biobased thermoset with tunable extended network. *Eur. Polym. J.*. **2016**, *81*, 33710.1016/j.eurpolymj.2016.06.018.

(57) Spontón, M.; Ronda, J. C.; Galià, M.; Cádiz, V. Studies on thermal and flame retardant behaviour of mixtures of bis(m-aminophenyl)methylphosphine oxide based benzoxazine and glycidylether or benzoxazine of Bisphenol A. *Polym. Degrad. Stab.*. **2008**, *93* (12), 215810.1016/j.polymdegradstab.2008.08.004.

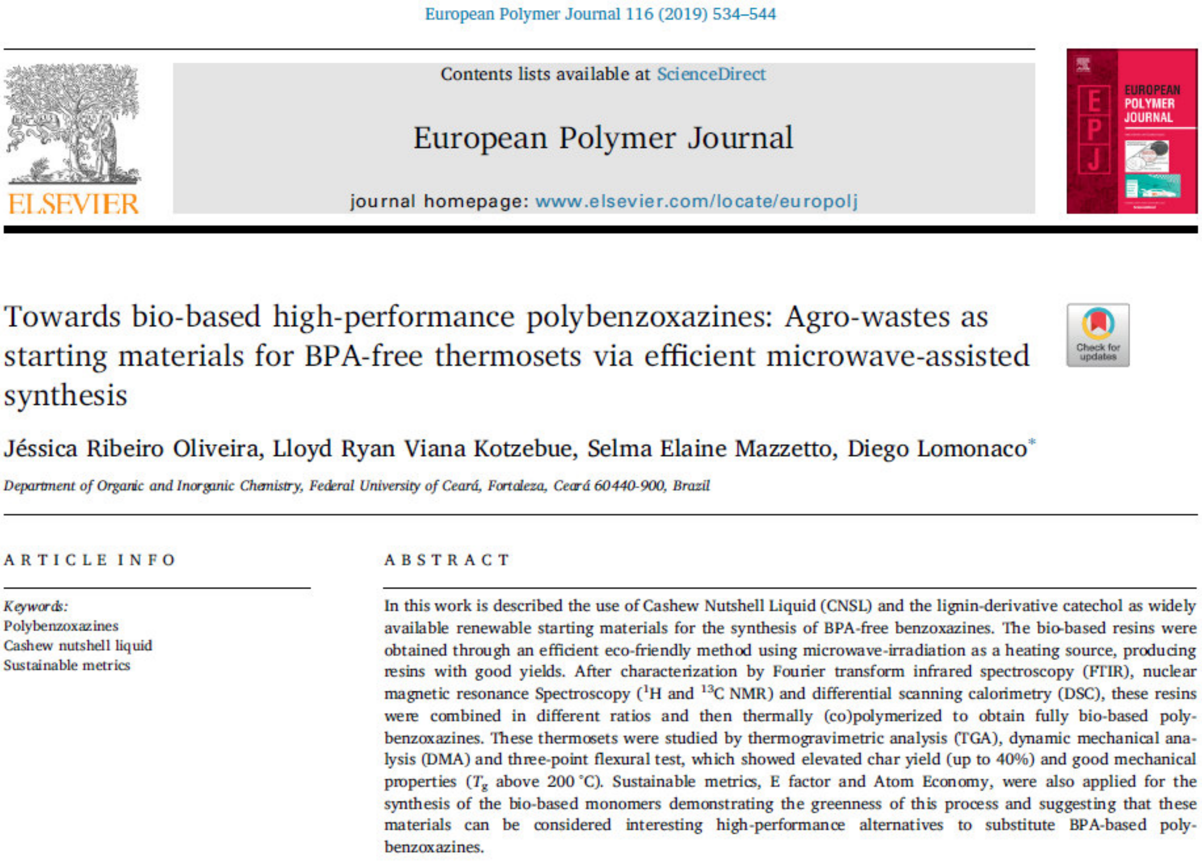
(58) Shabestari, M. E.; Kalali, E. N.; González, V. J.; Wang, D.-Y.; Fernández-Blázquez, J. P.; Baselga, J.; Martin, O. Effect of nitrogen and oxygen doped carbon nanotubes on flammability of epoxy nanocomposites. *Carbon.* **2017**, *121*, 19310.1016/j.carbon.2017.05.087.

(59) Fang, Y.; Zhou, X.; Xing, Z.; Wu, Y. Flame retardant performance of a carbon source containing DOPO derivative in PET and epoxy. *J. Appl. Polym. Sci.*. **2017**, *134* (12), 10.1002/app.44639.

(60) Bereska, A.; Kafarski, P.; Bereska, B.; Tkacz, B.; Iłowska, J.; Lenża, J. The application of organophosphorus flame-retardants in epoxy resin. *J. Vinyl Addit. Technol.*. **2017**, *23* (2), 14210.1002/vnl.21492.

(61) Hill, D. J. T.; Perera, M. C. S.; Pomery, P. J.; Toh, H. K. Dynamic mechanical properties of networks prepared from siloxane modified divinyl benzene pre-polymers. *Polymer* **2000**, *41* (26), 913110.1016/S0032-3861(00)00260-3.

ATTACHEMENT B – TOWARDS BIO-BASED HIGH-PERFORMANCE POLYBENZOXAZINES: AGRO-WASTES AS STARTING MATERIALS FOR BPA-FREE THERMOSETS VIA EFFICIENT MICROWAVE-ASSISTED SYNTHESIS”



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Towards bio-based high-performance polybenzoxazines: Agro-wastes as starting materials for BPA-free thermosets via efficient microwave-assisted synthesis

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ARTICLE INFO

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ABSTRACT

In this work is described the use of Cashew Nutshell Liquid (CNSL) and the lignin-derivative catechol as widely available renewable starting materials for the synthesis of BPA-free benzoxazines. The bio-based resins were obtained through an efficient eco-friendly method using microwave-irradiation as a heating source, producing resins with good yields. After characterization by Fourier transform infrared spectroscopy (FTIR), nuclear magnetic resonance Spectroscopy (^{1}H and ^{13}C NMR) and differential scanning calorimetry (DSC), these resins were combined in different ratios and then thermally (co)polymerized to obtain fully bio-based polybenzoxazines. These thermosets were studied by thermogravimetric analysis (TGA), dynamic mechanical analysis (DMA) and three-point flexural test, which showed elevated char yield (up to 40%) and good mechanical properties (T_g above 200 °C). Sustainable metrics, E factor and Atom Economy, were also applied for the synthesis of the bio-based monomers demonstrating the greenness of this process and suggesting that these materials can be considered interesting high-performance alternatives to substitute BPA-based polybenzoxazines.

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1. Introduction

The constant search to develop new bio-based polymers is a current trend among the scientists that seek ways to contribute heavily with the circular economy. The growing rigorous laws of environmental agencies and environmental awareness of consumers turned bio-based thermosets as one of the most studied renewable polymers, due to the low cost and the global availability of biomass as starting material, with applications that range from adhesives to high-performance polymers [1]. The most known bio-based thermosets are phenolics [2,3], polyurethanes [4–6] and epoxies [7] which uses mostly vegetable oils, cardanol and lignin derivates as starting material. But another class of polymers that have entered this field to dispute with these renewable polymers are polybenzoxazines, which are polymeric products of benzoxazines.

Benzoxazines are a class of high performance thermosetting resins that have attracted the attention of industrial and academic sectors due to their peculiar properties, such as: easy thermal curing by ring-opening polymerization, in which the use of catalysts or hardeners is not required, low thermal expansion, high glass transition temperature (T_g), low moisture absorption, good chemical resistance and improved thermal and mechanical properties [8–10]. Another very attractive characteristic from the synthetic point of view is the great molecular design flexibility, since the synthesis of these monomers occurs from a phenolic compound, a primary amine and formaldehyde, making it possible to use a wide variety of starting materials, including derivatives of renewable feedstock [11].

Phenolic compounds are described as the most studied starting materials in the literature of benzoxazines. Additionally, one of the richest and natural sources of these compounds is the Cashew Nutshell Liquid (CNSL), localized in the honeycomb of the cashew nutshell (*Anacardium occidentale* L.) [12]. The *natural* CNSL possesses a chemical composition of anacardic acid (71.70–82.00%), cardol (13.80–20.10%), cardanol (1.60–9.20%) and 2-methyl cardol (1.65–3.90%) [13], but due to the elevated temperatures during the almond processing of the cashew nut industries, the anacardic acid suffers a decarboxylation reaction, turning this CNSL rich in cardanol [12]. This CNSL, also called as *technical* CNSL, is the main by-product after the industrial processing of the cashew almond and it possesses a chemical composition of cardanol (67.82–94.60%), cardol (3.80–18.86%), anacardic acid (1.09–1.75%), 2-methyl cardol (1.20–4.10%) and polymeric materials (0.34–21.63%) [13].

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Considering that in 2016 the world production of cashew nuts *in natura* was almost 5 million tons [14], and knowing that CNSL represents around 25% in weight of the nut [15], it can be estimated that around 1.25 million tons of CNSL could be produced on that year. This large quantity of by-product, aligned with the chemical versatility of the phenolic compounds and the low cost, makes CNSL a very promising and renewable raw material for the development of new bio-based benzoxazines [16].

Another interesting agro-industrial waste is lignin, an amorphous heterogeneous macromolecule localized in the cell walls of vascular plants, which its main usage is to provide protection against biochemical interventions by avoiding enzymatic reactions of inner components [17]. Being considered as the second most abundant biopolymer, lignin consists of a complex structure containing mainly three units: guaiacyl (G), *p*-hydroxyphenyl (H) and syringyl (S) [18]. According to Laurichesse and Avérous [17], the global availability of lignin can exceed 300 billion tons and only the pulp and paper industries produced around 50 million tons in 2010. The immense availability of this feedstock has put scientists to dedicate a lot of efforts to depolymerize lignin into phenylpropanoids, as these are considered to be very interesting for the production of a various value-added bioaromatics such as vanillin, guaiacol and catechol [19–21].

Previously, it was demonstrated that catechol is a promising renewable phenolic compound to synthesize bis-benzoxazine (**CT-fu**) making it suitable for producing high thermal and mechanical resistant thermosets with glass transition temperatures (T_g) above 250 °C [22].

Benzoxazines synthesized from CNSL-based phenols are reported in the literature and their polymers demonstrated interesting thermal properties [15,23]. However, due to the low values of storage moduli (E') and the T_g, the thermo-mechanical properties of CNSL-based polybenzoxazines turn them not so desired for high-performance applications [23,24]. The reason that these polybenzoxazines possess these properties is mainly due to the great mobility of long aliphatic chains of their respective phenols, which suggests a low crosslinking density of the polymer [23,24].

A strategy already reported in the literature to improve the mechanical properties of the cardanol-based polybenzoxazines is the functionalization of the instaurations on the aliphatic chain, such as epoxidation [25]. Ambrožič and coworkers demonstrated that the epoxy-functionalized polybenzoxazine had a storage modulus almost twice as high as of the conventional cardanol-based polybenzoxazines [25]. On the other hand, the glass transition temperature (T_g) reported did not increase significantly, which was from 89 to 110 °C [25]. Due to these low T_g and to the reactivity of the epoxy groups, that can react with primary amines during the benzoxazines synthesis, another strategy to increase the thermo-mechanical properties of CNSL-based polybenzoxazines is still recommended.

An alternative to obtain polybenzoxazine with good thermal and mechanical properties, is by increasing the number of oxazine rings in a monomer, such as bis-benzoxazines, which could increase significantly the crosslinking in the polymer matrix [11]. As cardanol-based benzoxazines are generally monofunctional, a strategy to use this monomer for high-performance thermosets is its (co)polymerization with a bis-benzoxazine. Kotzebue and co-workers performed a study of copolymerization with catechol- and BPA-based bis-benzoxazines (**CT-fu** and **BA-fu**, respectively) and it was observed that the insertion of **CT-fu** greatly improved the properties of the copolymer [22].

Therefore, considering the renewability of catechol and furfurylamine [26,27], the main purpose of this work is to synthesize highly bio-based benzoxazines from non-edible CNSL and improve the thermal and mechanical properties of its polybenzoxazine by (co)polymerizing it with catechol-based bis-benzoxazine.

After the structural and thermal characterization of benzoxazine monomers obtained by Fourier transform infrared spectroscopy (FTIR), ^{1}H and ^{13}C nuclear magnetic resonance spectroscopy (NMR), and differential scanning calorimetry (DSC), the copolymers were investigated by thermogravimetric analysis (TGA), dynamic (DMA) and static mechanical analysis.

2. Experimental

2.1. Materials

Technical CNSL (Cashew nutshell liquid) was supplied by Amêndoas do Brasil LTDA. Catechol (99%), furfurylamine (99%) and paraformaldehyde (99%) were used as received from Sigma-Aldrich. PEG (Kollisolv® PEG E 400) was used as received from Aldrich. Ethyl acetate, dichloromethane, methanol, sodium hydroxide and anhydrous sodium sulphate, were used as received from LabSynth (Brazil).

2.2. Synthesis and analytical methods

2.2.1. Microwave-assisted organic synthesis

The microwave-assisted organic synthesis was performed in a Milestone microwave reactor, model StartSYNTH, operating in an open-vessel configuration at a frequency of 2.45 GHz. The temperature set was controlled by a contact-less infrared sensor, and the power applied was limited to 500W.

2.2.2. Fourier transform infrared spectroscopy (FTIR)

The FTIR spectra were obtained using a Perkin Elmer FTIR/NIR FRONTIER spectrometer, using attenuated total reflectance (ATR) fixture with zinc selenide crystal surface (ZnSe), and resolution of 4 cm^{-1} using the arithmetic average of 32 scans in the wavenumber range of 4000–550 cm^{-1}.

2.2.3. ^{1}H and ^{13}C nuclear magnetic spectroscopy (^{1}H and ^{13}C NMR)

The ^{1}H NMR and ^{13}C NMR spectra were obtained on a BRUKER, Avance DPX model spectrometer, operated at a frequency of 300 MHz for ^{1}H and of 75 MHz for ^{13}C. Deuterated chloroform ($CDCl_3$) was used to dissolve the samples, and tetramethylsilane (TMS) was used as an internal standard.

2.2.4. Differential scanning calorimetry (DSC)

The DSC analyses were made using a Mettler-Toledo DSC 823e, using 5 mg samples in aluminium pans. Non-isothermal measurements were made with a heating rate of 10 °C min^{-1}, in a temperature range of 30–400 °C, under nitrogen (N_2) purge at a flow rate of 50 mL min^{-1}.

2.2.5. Thermogravimetric analyses (TGA)

The TGA analyses were carried out using a Mettler-Toledo TGA/SDTA851e using 5 mg samples placed in an alumina pan. The measurements were performed from 30 °C to 800 °C, at a scanning rate of 10 °C min^{-1} under nitrogen (N_2) atmosphere at a flow rate of 50 mL min^{-1}

2.2.6. Dynamic mechanical analyses (DMA)

DMA were conducted on a Mettler-Toledo DMA-1, using a single cantilever mode, at a heating rate of 3 °C min^{-1} from 30 to 250 °C, and a frequency of 1 Hz under air. The deformation applied was within the linear viscoelastic limit, determined by a strain sweep test.

2.2.7. Mechanical analysis

A three-point bending test was performed using a universal testing machine Instron (Instron, model 3345, Canton, USA). The crosshead speed was set at 0.5 mm/min and one sample of each polybenzoxazine, with 80 mm × 4.3 mm × 1.3 mm dimension, was used with a useful length of 70 mm.

2.2.8. Method for microwave-assisted synthesis of **CNSL-fu**

In a 125 mL round-bottom flask equipped with a stirring bar was added CNSL (20.00 g), paraformaldehyde (5.60 g, 184.8 mmol) and furfurylamine (7.25 g, 73.9 mmol). The flask was placed in the microwave and fitted with a 50 cm Vigreux column and distillation head. The microwave was programmed to increase from room temperature to 100 °C for 5 min, using maximum power of 500 W. After the stabilization of the temperature, the reaction continued for more 5 min. At the end of the reaction, the material was cooled to room temperature. The reaction mixture was diluted with ethyl acetate (250 mL) and this organic solution was washed in a separating funnel with an aqueous solution of 2 mol L^{-1} NaOH (3 × 150 mL) and with distilled water (3 × 150 mL). Finally, the organic phase was collected, dried over sodium sulphate, filtered, concentrated under reduced pressure and a dark brown viscous liquid was obtained 24.84 g. The chemical structures were characterized by ^{1}H NMR, ^{13}C NMR and FTIR and compared with the previous published results [28] indicating the success of the procedure.

RMN ^{1}H ($CDCl_3$, 300 MHz, δ) 7.4162 (s,1H), 6.8444 (d, 7.6 Hz,1H), 6.7315 (d, 7.7 Hz, 1H), 6.6502 (s, 1H), 6.3382 (m, 2H), 5.3567 (m, 3H), 5.0030 (m, 1H), 4.8705 (m, 2H), 3.9927 (s, 2H), 3.9282 (m, 3H), 2.7972 (m, 2H), 2.5408 (t, 7.6 Hz, 2H), 2.0476 (m, 4H), 1.5996 (m, 2H), 1.3219 (m, 15H), 0.8914 (m, 2H).

RMN ^{13}C ($CDCl_3$, 75 MHz, δ): 153.92, 153.52, 151.93, 144.35, 143.12, 142.71, 141.61, 137.00, 132.05, 130.58, 130.13, 130.02, 129.49, 128.51, 128.36, 128.20, 128.03, 127.78, 127.55, 127.02, 121.66, 121.23, 117.33, 116.91, 116.37, 115.19, 114.88, 110.53, 110.35, 109.06, 107.25, 81.96, 56.54, 49.64, 48.40, 39.06, 35.87, 31.97, 31.71, 31.49, 29.95, 29.93, 29.82, 29.59, 29.49, 29.40, 29.17, 27.42, 27.39, 25.85, 25.77, 22.98, 22.84, 14.28, 13.98.

FTIR (ATR-ZnSe, cm^{-1}): 1578 (stretching of furan ring), 1504 (stretching of trisubstituted benzene ring), 1240 (C—O—C asymmetric stretching), 915 (benzoxazine related mode).

2.3. *Method for microwave-assisted synthesis of* ***CT-fu*** *(3,8-bis(furan-2-ylmethyl)-2,3,4,7,8,9-hexahydrobenzo[1,2-e:4,3-e']bis([1,3]oxazine)*

CT-fu was synthesized using a modified method as published previously by our group [22]. In a 250 mL round-bottom flask equipped with a stirring bar was added PEG (50 mL) and then heated until 80 °C. Catechol (10.00 g, 89.91 mmol), paraformaldehyde (13.62 g, 449.55 mmol) and furfurylamine (17.64 g, 179.82 mmol) were added into the hot PEG and then stirred for 3 min to form a light red suspension. The flask containing the mixture was placed in the microwave and fitted with a 50 cm Vigreux column and distillation head. The Microwave was set to a maximum power of 500 W, temperature was programmed to increase from 60 to 120 °C in a period of 2 min; and kept at this temperature for additional 5 min, totalling 7 min under microwave irradiation. After the completion of the reaction, the mixture was put to cool till room temperature forming a bulky solid phase. The reaction mixture was washed with 100 mL of methanol and transferred to an Erlenmeyer (250 mL). The mixture was sonicated in an ultrasound bath (40 kHz) at 40 °C for 2 h and then a vacuum filtration was performed. The residue was washed once more and then put to dry in an oven at 80 °C to overnight for solvent evaporation, obtaining a 23.15 g (72% yield) white powder. The chemical structures were characterized by ^{1}H NMR, ^{13}C NMR and FTIR.

RMN ^{1}H ($CDCl_3$, 300 MHz, δ) 7.42 (d, 2 Hz, 1H), 6.51 (s, 1H), 6.34 (m, 1H), 6.27 (m, 1H), 4.99 (s, 2H), 4.00 (s, 2H), 3.970 (s, 2H,);

RMN ^{13}C ($CDCl_3$, 75 MHz, δ): 151.8, 142.7, 119.0, 118.7, 110.4, 109.1, 82.7, 49.3, 48.6;

FTIR (ATR-ZnSe, cm^{-1}): 1577 (stretching of furan ring), 1478 (stretching of tetrasubstituted benzene ring), 1235 (C—O—C asymmetric stretching), 923 (benzoxazine related mode).

2.3.1. *(Co)polymerization of the bio-based benzoxazines*

CNLS-fu and the combined mixtures with **CT-fu**, as described in Table 1, were put in silicone molds (40 × 20 × 2 mm) and melted at 140 °C in a vacuum oven. The polybenzoxazines were obtained using the following heating ramp: 140 °C for 1 h, 160 °C for 1 h, 180 °C for 1 h and 200 °C for 2 h. A post-cure treatment was performed at 220 °C for 2 h and 240 °C for 2 h. The sample mass used in the polymerization was approximately 1.5 g.

Table 1
Composition of bio-based bis-benzoxazine resins.

Sample	CT-fu (wt %)	CNSL-fu (wt %)
CNSL/CT10	10	90
CNSL/CT20	20	80
CNSL/CT 30	30	70
CNSL/CT 40	40	60
CNSL/CT 50	50	50

3. Results and discussion

3.1. *Microwave-assisted synthesis of CNSL-fu and CT-fu*

Bearing in mind the wide application of the benzoxazines resins in the industrial and academic sectors for polymeric materials, which usually require large quantities of starting material for its production and considering this with environmental concerns, the use of widely available eco-friendly resources has induced great interest [29–32]. In this sense, CNSL and catechol were chosen as starting materials for the development of polybenzoxazines in this work.

The benzoxazines monomers derived of CNSL and catechol synthesized with the furfurylamine were obtained by means of a one-step reaction and under microwave irradiation (Scheme 1).

Microwave-assisted synthesis of bio-based benzoxazines has been reported in the literature as highly efficient procedure. This synthesis has low reaction times and similar or higher yields when compared to traditional heating [22,33].

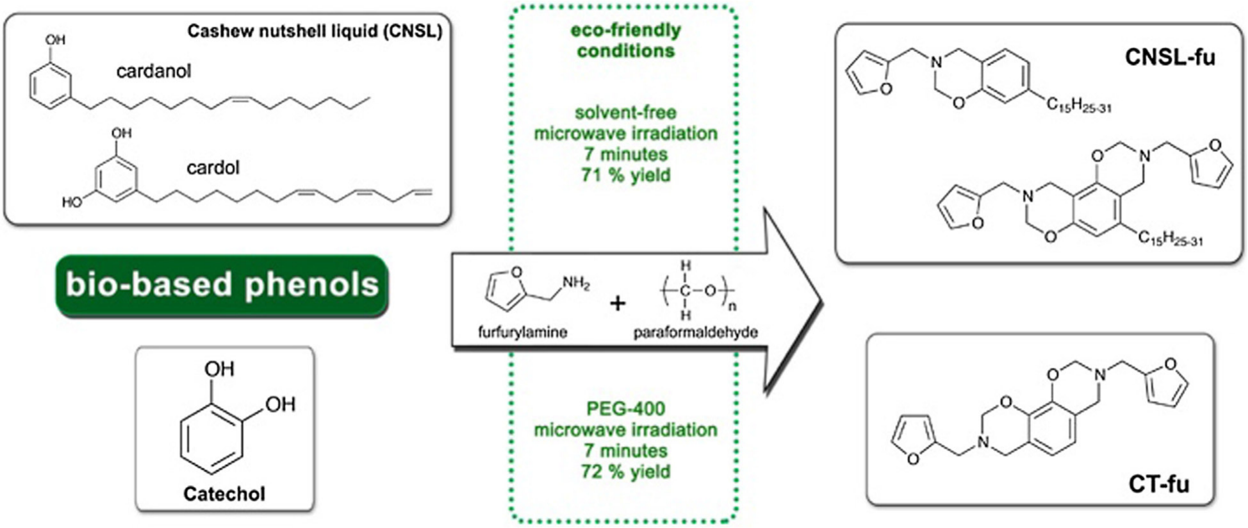
The efficiency of the microwave-assisted synthesis can be attributed to the interaction between organic molecules with the electric component of the microwave irradiation. The phenomenon of warming promoted by irradiation of microwaves resides in the dielectric heating, which is the ability of some compounds to transform electromagnetic energy into heat [34]. This ability is closely related to the polarity of these compounds.

CNSL is mainly composed by cardanol (81%), cardol (15%) and minor quantities of 2-methyl cardol, compounds that present an aliphatic side-chain containing up to 3 unsaturations [16]. For the **CNSL** employed in this work, the majority of cardanol was found as monounsaturated (80%) compound, while cardol as triunsaturated (63%) one. Therefore, **CNSL-fu** was composed by both mono- and bis-benzoxazines, as depicted in Scheme 1.

The bio-based benzoxazine resin **CNSL-fu** was obtained from **CNSL**, furfurylamine and paraformaldehyde in conditions of complete absence of solvents, since, except for paraformaldehyde, the reagents are liquids at room temperature, providing the complete solubilization of the reaction medium. The fast synthesis of **CNSL-fu** under microwave irradiation in just 7 min proved to be very promising, once it is reported in the literature that the synthesis of benzoxazines monomers from cardanol are usually obtained with reaction times lasting hours or days [23,25,28].

Catechol-based benzoxazine (**CT-fu**) was obtained as related in the literature [22], starting from catechol, furfurylamine and paraformaldehyde, and with the use of PEG as a nontoxic solvent. The synthesis of catechol-based benzoxazine under microwaves irradiation proved again to be very promising, due to shorter reaction time (7 min), compared with other bis-benzoxazine syntheses using traditional heating methods and toxic solvents, with reaction times of around 24 h [35].

It is worth emphasizing the importance of obtaining benzoxazines resins in large quantities, once it is used in the field of polymer and



Scheme 1. Synthesis of benzoxazine monomers CNSL-fu and CT-fu.

materials science. The use of sources with a high amount of feedstock to obtain new bio-based benzoxazines, and a versatile methodology that requires a few minutes of reaction and generates good amounts of material, is a promising study with great potential to be exploited in a vast area of the science of polymers and materials.

3.2. Structural characterization of bio-based benzoxazines

In order to determine the purity and the chemical structure of benzoxazines synthesized from CNSL and catechol, the obtained products were investigated by FTIR and ^{1}H NMR.

Fig. 1 shows the FTIR spectra of the CNSL and its respective benzoxazine. In the spectrum of the benzoxazine monomer (**CNSL-fu**), the absence of the band at 3351 cm^{-1}, assigned to the O–H bond stretching, indicated the transformation of the hydroxyl group. The band at 1578 cm^{-1} was attributed to the vibrational mode of the furan ring [35]. The absorption band at 1504 cm^{-1} was referred to the C=C stretching of the trisubstituted benzene ring [36] of the cardanol-derived benzoxazine of **CNSL-fu**. In addition, the formation of the fused oxazine ring on the benzene ring was confirmed by the appearance of the absorption bands at 1239 cm^{-1}, referred to the =C–O–C group, and by the band at 915 cm^{-1}, a vibrational mode characteristic to benzoxazines [36].

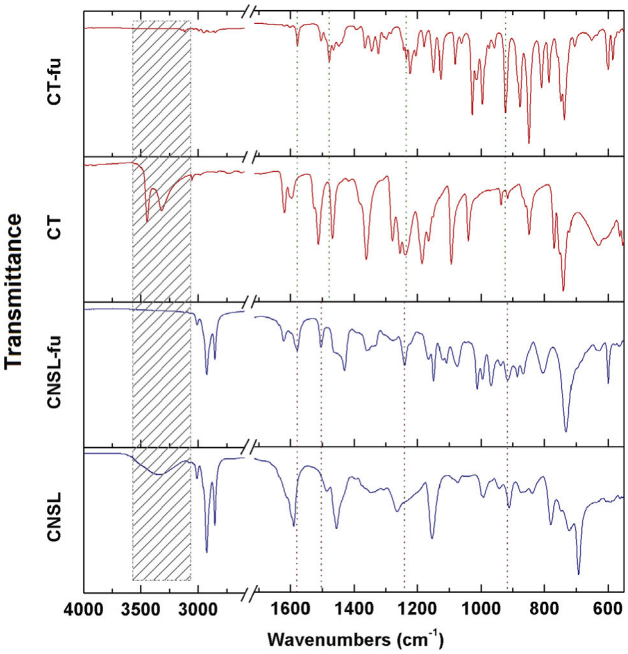


Fig. 1. FTIR spectra of CNSL, catechol (CT) and their benzoxazine derivatives (CNSL-fu and CT-fu).

The structure of the benzoxazine monomer **CT-fu** was also confirmed by FTIR (Fig. 1). The absence of the broad band at 3441 cm^{-1}, attributed to the of the O–H bond stretching, indicates the transformation of the hydroxyl group. The 1579 cm^{-1} band is attributed to the vibrational mode of the furan ring [35], and the presence of the oxazine ring is indicated by the bands 1478, 1235 and 923 cm^{-1} assigned to the C=C stretch of the tetra-substituted benzene ring, to asymmetric stretching =C–O–C and to benzoxazine related mode, respectively.

More detailed structural information was obtained of the synthesized monomers, **CNSL-fu** and **CT-fu**, through ^{1}H NMR analyses.

For the benzoxazine characterization by ^{1}H NMR, the identification of the methylene hydrogens of the oxazine rings are of most importance. The peaks observed at 4.79 to 4.93 ppm and at 3.90 to 3.96 ppm are attributed to the O-$\mathbf{CH_2}$-N and the Ar-$\mathbf{CH_2}$-N hydrogens, respectively, which indicated the formation of the oxazine rings. The aliphatic chains of the benzoxazines were observed by the peaks at the range of 0.80–2.90 ppm, representing the alkyl groups, and by the peaks at the range of 4.95–5.95 ppm, representing the olefinic groups. The peaks observed at 6.20–7.50 ppm are referred to the aromatic hydrogens (Fig. 2).

Analyzing the aromatic region (Fig. 2), it was possible to perform a semi-quantitive analysis of the composition of cardanol- and cardol-based benzoxazines in **CNSL-fu**. Specific individual peaks related to each of the two monomers were identified by the doublet at 6.87 ppm, referred to the hydrogen **i** of the cardanol-based benzoxazine, and the singlet at 6.31 ppm, referred to the solely benzene hydrogen **g'** of the cardol-based bis-benzoxazine [28]. After comparing the integrals of the peaks related to hydrogen **i** with hydrogen **g'** of 1.00 and 0.35, respectively, it was estimated that **CNSL-fu** was composed of around 26% (mol/mol) of cardol-based benzoxazine. This estimated composition of the bis-benzoxazine was also confirmed by analyzing the integrals of the peak of hydrogen **i** with the peaks referred to the α- and β-hydrogens of the furan groups (**a**, **a′**, **b**, **b′**, **c** and **c′**) of the two monomers.

3.3. Sustainable metrics of benzoxazine syntheses

Looking forward to evaluating the "greenness" of these two benzoxazine monomers, we also investigated their synthetic processes

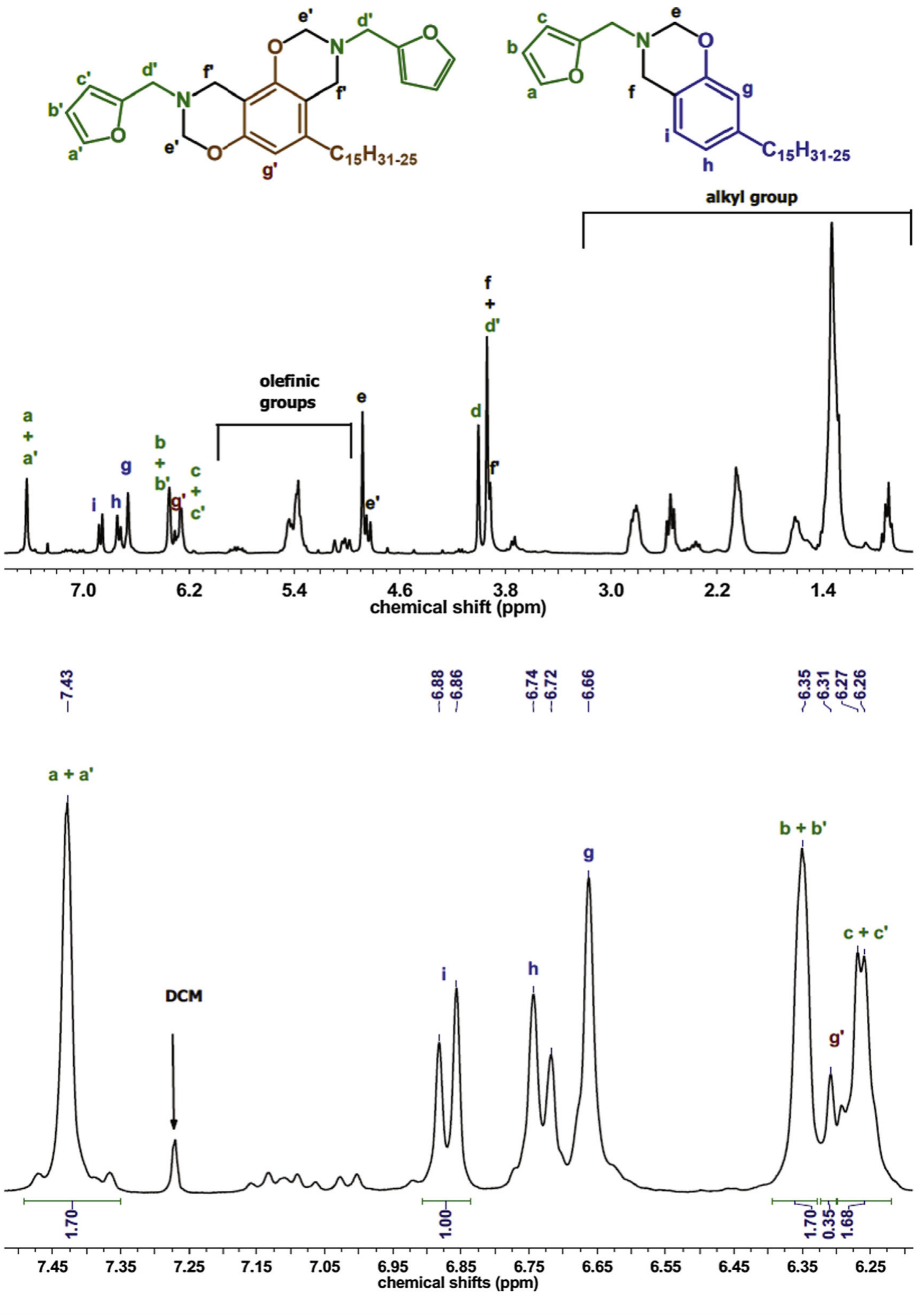


Fig. 2. ^{1}H NMR spectra of CNSL-fu.

Table 2
Sustainable metrics of the syntheses of benzoxazine resins.

Benzoxazine	AE (%)	E-factor
CNSL-fu	~ 90	11.23
CT-fu	83	10.05

based on the two most known sustainable metrics: Atom Economy (AE) and Environmental Factor (E factor) [37]. The detailed calculations of these sustainable metrics are available as Supporting Information while the obtained values are summarized in Table 2.

To the best of our knowledge, this is the first time in which sustainability indicators are applied for the syntheses of benzoxazine resins.

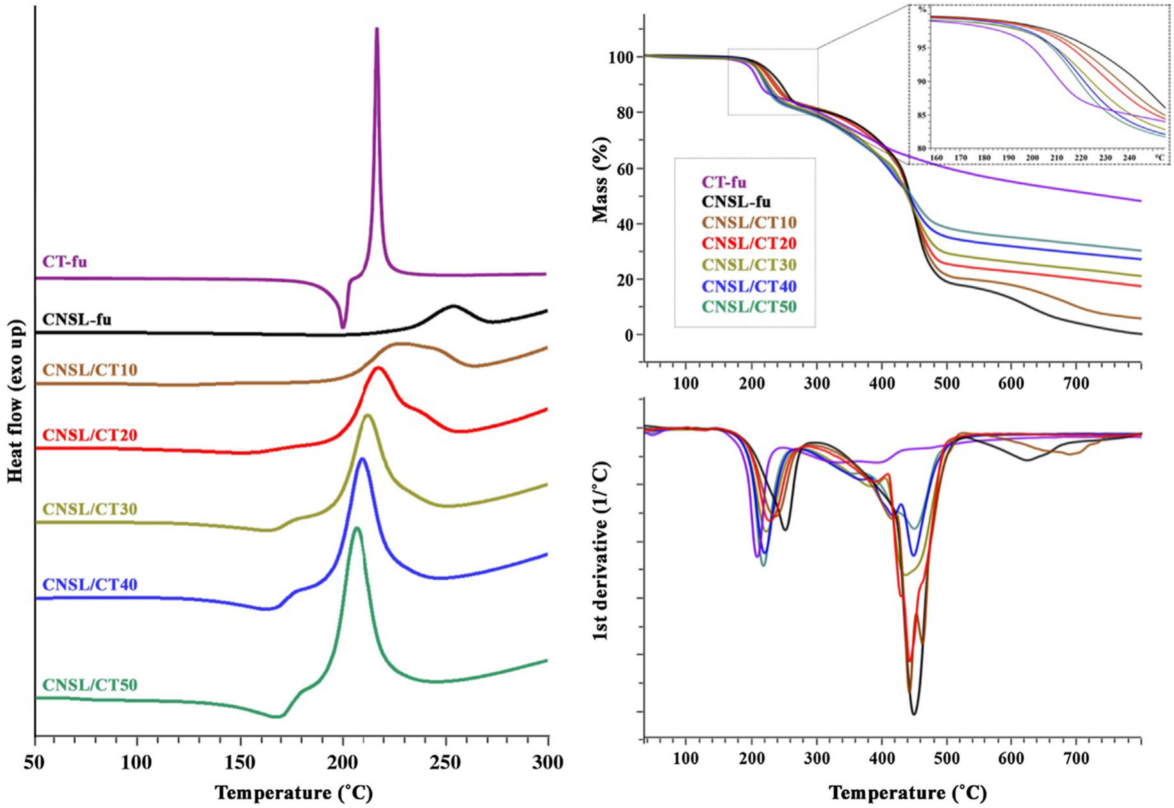


Fig. 3. DSC and TGA curves of CNSL-fu and CT-fu monomers and mixtures.

3.3.1. Atom Economy (AE)

Being part as one of the twelve principles of *Green Chemistry*, Atom Economy is the simplest and most known sustainable metric [38]. According to Trost, AE can be understood as how much of the reactants is part of the product [39], in other words, it is the ratio of the molar weight of the product by the sum of the molar weights of the reactants.

The ideal AE value is 100%, meaning that all the reactants used ended up in the product. Using this concept for the benzoxazine syntheses of this work, it was observed that their AE values were at least 83%. Because of the loss of at least two water molecules, it can be concluded that benzoxazine reactions can be overall quite sustainable. And the higher the molecular weights of the chosen phenolic compound and/or primary amine, the higher the AE values, as it was observed for the synthesis of **CNSL-fu**.

3.3.2. Environmental factor (E factor)

Atom Economy has one main disadvantage, which is, it cannot determine the amount of waste produced during a reaction. Therefore, another sustainable index was used in order to overcome this drawback and provide more consistent information about benzoxazine synthesis sustainability.

Prof. Roger Sheldon came up with an interesting metric called Environmental Factor, or also known as the "*E* factor", which is a useful way to quantify the waste production of a chemical process [37,40]. The *E* factor is calculated by taking into account the mass of all materials used in the whole process, minus the mass of the desired product, divided by the mass of the desired product. An exception that has been taken is water, since counting this would lead to very high and unreasonable *E* factor results [37]. The lower this factor, the more sustainable the process is considered. The ideal *E* factor value would be zero.

This sustainable metric was used for the two benzoxazine syntheses of **CNSL-fu** and **CT-fu**, demonstrating that their *E* factors were around 11, classifying them in the industry segment of fine chemicals [37]. Unfortunately, the *E* factors of the two benzoxazine syntheses methods may not be compared between them, as the processes used and the obtained products are not the same. However, the production of benzoxazine resins can be highly sustainable for thermoset applications, where further purifications of these resins are not necessarily required. Using as an example the benzoxazine synthesis method of **H-Fa** and **R-Fa** of Dumas and coworkers [27], no work up were performed after the completion of the reactions, demonstrating that benzoxazine synthesis can reach very low E factors.

Using Atom Economy and Environmental factor for the benzoxazine syntheses of **CNSL-fu** and **CT-fu** demonstrated to be important to have an idea how sustainable these methods are. And it was also understandable which variables can be altered when seeking for a more sustainable pathway to synthesize the resin of choice.

Nevertheless, some parameters of the benzoxazine syntheses of **CNSL-fu** and **CT-fu** were not considered in these metrics but are worth to be mentioned, since they indicate that these resins and methods can be even more sustainable than as demonstrated by the metrics, which are:

1. CNSL and lignocellulosic feedstocks as starting materials (low-cost, widely available, no food-chain hampering issues);
2. Methods employed solvent-free system or atoxic PEG as solvent;
3. Microwave-assisted heating (effective and fast heating, meaning higher energy saving);
4. Recyclability of solvents used (ethyl acetate and methanol).

3.4. Polymerization behavior of bio-based copolymers

Non-isothermal differential scanning calorimetry (DSC) analyses were performed of **CNSL-fu** and its mixtures with **CT-fu**, prepared in various molar ratios, to provide a better understanding of the polymerization behavior of each sample (Fig. 3). **CT-fu** monomer was not analyzed for this work, as it has already been reported previously [22].

Table 3
DSC and TGA data from CNSL-fu and its mixtures with CT-fu.

Monomers	DSC					TGA		
	T_m (°C)	T_e (°C)	T_p (°C)	Oxazine ring (mmol/g)	ΔH (J/g)	T_e (°C)	T_5 (°C)	Char yield (%)
CNSL-fu	–	233	253	2.66	16.8	209	221	0
CNSL/CT10	–	205	225	2.95	49.0	206	218	5.4
CNSL/CT20	–	201	217	3.25	77.2	203	215	17.0
CNSL/CT30	165	199	212	3.56	95.5	201	209	20.7
CNSL/CT40	164	197	209	3.87	118.8	201	208	27.7
CNSL/CT50	168	195	206	4.17	136.4	201	207	29.8
CT-fu^{22}	198	213	220	5.7	381.0	192	199	47.6

The initial (T_e) and maximum (T_p) polymerization temperatures as well as the melting points (T_m) of bio-based benzoxazines and mixtures are summarized in Table 3.

In the DSC thermograms of **CNSL-fu** it was observed two exothermic events as expected for typical cardanol-based benzoxazines. The first exothermic event, between 220 and 280 °C, is regarded to the ring-opening polymerization of the oxazine ring and the second event, between 280 and 400 °C, is referred to the polymerization of the olefinic groups of the aliphatic chains. The T_p of **CNSL-fu** was 10 °C lower than the Ca-FA-BOX of Ambrožič and co-workers [25], which used pure cardanol and furfurylamine as starting materials. Despite that **CNSL-fu** is mainly constituted of cardanol-based benzoxazines, the presence of cardol-based benzoxazines, which are bis-benzoxazines, may be promoting the polymerization to occur at lower temperatures.

Considering that CNSL-based benzoxazines demonstrate low mechanical properties and **CT-fu** is extremely difficult to be homopolymerized due to its narrow processing window, as reported in a previous work [22], it was proposed to mix the liquid **CNSL-fu** and the solid **CT-fu** in different ratios, looking forward obtaining a more processable high-performance bio-based polybenzoxazine. The relation of the ratios of the mixed resins and the thermal and thermomechanical properties of their respective copolymers was also investigated.

Analyzing the polymerization behavior of the mixtures, no endothermic events were observed on **CNSL/CT10** and **CNSL/CT20**, demonstrating that **CT-fu** was well dissolved in **CNSL-fu**, and the good compatibility between monomers. On the other hand, the DSC curves of the other systems (**CNSL/CT30**, **CNSL/CT40** and **CNSL/CT50**) presented small endothermic events at around 150–180 °C, indicating the presence of insoluble **CT-fu** in the mixtures. Nevertheless, as the melting enthalpy of these mixtures are very low, it is possible that these resins will provide imperfect-free copolymers after curing.

After analyzing the exothermic events of the mixtures, it was observed that by increasing their **CT-fu** content, the initial polymerization temperature (T_e) and maximum (T_p) temperature of the mixtures decreased gradually, demonstrating that the ROP process is initiated predominantly by **CT-fu** reacting further with the other monomers (Scheme 2). This behavior was also observed in a previous work [22].

Another interesting observation was the increase of the polymerization enthalpy (Δ*H*) of the systems with the increasing content of **CT-fu**. This results can be correlated to the oxazine-ring concentration of each system (Tab. 3), since **CT-fu** has an elevated concentration of oxazine rings (mmols/gram) of monomers.

A previous work correlated the increase/decrease of the enthalpy of copolymerization of benzoxazine monomers with the formation of volatiles during the polymerization process [41]. In our work it is not the same case, since **CNSL-fu**, which has a lower Δ*H*, presented a higher boiling point than **CT-fu**, as observed by TGA analysis (Fig. 3 and Table 3).

After the thermal characterizations of the monomers and the mixtures, they, except for **CT-fu**, where (co)polymerized and then put to be post-cured as described in the Experimental section.

3.5. Evaluation of the thermal and mechanical properties of (co) polybenzoxazines

3.5.1. Thermogravimetric analysis (TGA)

The thermal stability of the **CT-fu/CNSL-fu** polybenzoxazines was studied by thermogravimetric analysis (TGA) under inert atmosphere (N_2) and their TGA curves are shown on Fig. 4. The obtained results of the polybenzoxazines are expressed in Table 4.

In the literature is described that cardanol-based benzoxazines have superior thermal stability when compared with BPA-based benzoxazines [42]. This observation was also confirmed in this work.

It was observed that **Poly(CNSL-fu)** had an impressive high thermal stability as it can be observed by its 5% weight loss temperature (T_5) of 381 °C, which was not expected as its polymer structure possesses a large number of aliphatic groups. By analyzing the influence of **CT-fu** in the copolymers (Table 3), it was observed that as the **CT-fu** content increased, the lower the T_5 of the polymers. Even though that **Poly(CNSL/CT50)** had de lowest T_5 among the polybenzoxazines, the 50% (w/w) increment reduced its 5% weight loss temperature only with 17 °C when compared with **Poly(CNSL-fu)**.

These fully bio-based polybenzoxazines possess good thermal stabilities in the initial phase of degradation when compared with BPA-based polybenzoxazines. For example, furan-BPA-based polybenzoxazines **P-BPA-FBz** [35] and **Poly(BA-fu)** [22] had a T_5 of 347 and 361 °C, respectively. And aniline-BPA-based polybenzoxazine of the commercially available **XU 35610** had a T_5 of 313 °C [43].

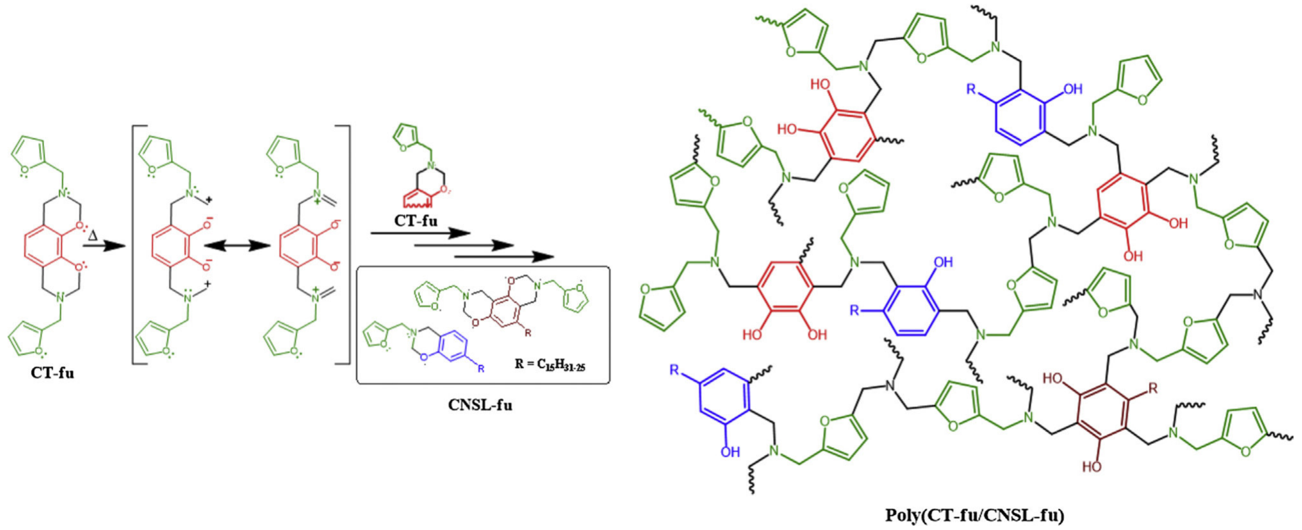
The insertion of the **CT-fu** monomer demonstrated that all the copolymers had an increase in the carbonization yield when compared to **Poly(CNSL-fu)**. For example, the **Poly(CNSL/CT50)** had a 36% increase in char yield when compared with **Poly(CNSL-fu)**. The **Poly (CNSL/CT40)** and **Poly(CNSL/CT50)** had higher char yields (at 800 °C) than of **Poly(BA-a)**, which ranges from 28.5 to 30.0% [44–46]. The fact that **Poly(CNSL/CT40)** and **Poly(CNSL/CT50)** possess high char yields could indicate that these copolymers have high flame retardancy properties.

And indeed, by using the van Krevelen equation [47] it was noticed that the estimated LOI values for **Poly(CNSL/CT40)** and **Poly(CNSL/CT50)** are 30.3 and 33.5, respectively. Knowing that materials with LOI values of > 28 are considered self-extinguishing [48], these two copolymers can be considered as a BPA-, halogen-, phosphor-, and silane-free fully bio-based flame retardants.

3.5.2. Mechanical analysis

The mechanical properties of the polybenzoxazines were analyzed using a 3-point bending mode and their respective stress-strain curves are shown in Fig. 5 and their data summarized on Table 5 and Fig. 7.

The stress-strain curves of the polybenzoxazines demonstrated only an elastic region, which is typical for brittle thermoset materials. Their high maximum flexural deformation (ε_f) could be attributed to the aliphatic chain which provides plasticity for the matrices. It was observed that with the increment of **CT-fu** in the polymer matrices, the higher was the flexural modulus (E_f) (Fig. 7), which was expected as



Scheme 2. Proposed copolymerization of CT-fu and CNSL-fu.

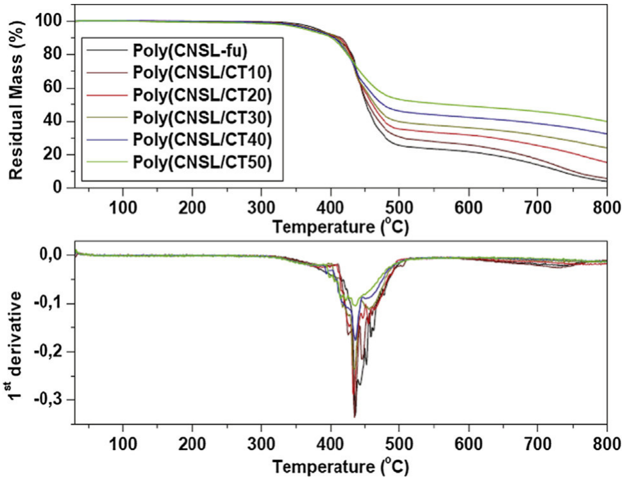


Fig. 4. TGA thermograms of (co)polybenzoxazines.

Table 4
Thermal properties of (co)polybenzoxazines obtained by TGA.

Polymer	T_5 (°C)	T_{max} (°C)	Char Yield (%)	LOI
Poly(CNSL-fu)	381	441	4	19.1
Poly(CNSL/CT10)	376	438	6	19.9
Poly(CNSL/CT20)	374	433	15	23.5
Poly(CNSL/CT30)	374	433	24	27.1
Poly(CNSL/CT40)	370	434	32	30.3
Poly(CNSL/CT50)	364	435	40	33.5

CT-fu is composed mainly of aromatic groups which increase the rigidity of the polymer. With the 50% increment of **CT-fu** in **poly(CNSL/CT50)**, the E_f of the polymer matrix was increased with 80%, when compared with **poly(CNSL-fu)**.

3.5.3. Dynamic mechanical analysis (DMA)

The thermo-mechanical properties of the polymers were analyzed by DMA (Fig. 6) and their data are expressed in Table 6, and Figs. 7 and 8.

It was observed that **Poly(CNSL-fu)** had a storage modulus (E') at 30 °C of 0.83 GPa, which is higher than the cardanol-based polybenzoxazine **pCDN-a** which had an E' of 0.54 GPa [23]. This increase of the storage modulus is due to the presence of the cardol-based benzoxazines, which is a bis-benzoxazine, as determined by ^{1}H NMR (Fig. 2) [28].

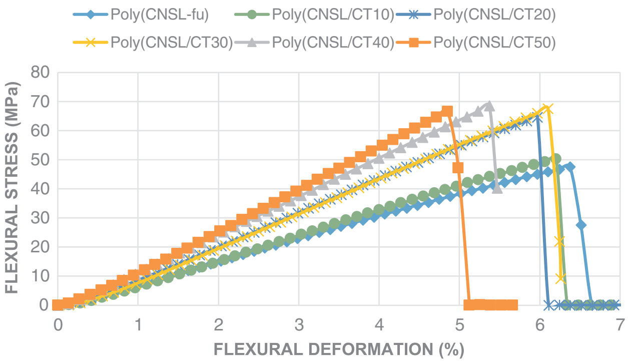


Fig. 5. Stress-strain curves obtained from 3-point bending of polybenzoxazines.

Table 5
Mechanical properties of polybenzoxazines obtained by 3-point bending mode.

Polymer	E_f (GPa)	σ_f (MPa)	ε_f (%)
Poly(CNSL-fu)	0.81	48	6.4
Poly(CNSL/CT10)	0.90	50	6.2
Poly(CNSL/CT20)	1.20	65	6.0
Poly(CNSL/CT30)	1.22	68	6.1
Poly(CNSL/CT40)	1.34	69	5.4
Poly(CNSL/CT50)	1.47	67	4.9

The presence of **CT-fu** in the copolymers altered significantly the mechanical properties of the polybenzoxazines. The higher the **CT-fu** content of the copolymers, the higher their storage modulus. At 30 °C (Figs. 6 and 7), all the copolymers demonstrated to have a E' above 1 GPa. By replacing 50% in weight the **CNSL-fu** with **CT-fu**, the storage modulus of the polymer was duplicated, as **Poly(CNSL/CT50)** showed a E' of 1.70 GPa. This fully bio-based copolymer presents itself as a promising BPA-free high-performance material. Analyzing the storage modulus of **Poly(CNSL/CT50)** at higher temperatures, it was observed that at 100 °C the E' of the polymer was still above 1 GPa, which is quite remarkable for cardanol-based polybenzoxazines.

The glass transition temperature (T_g) was determined by the peak maximum of the α-transitions (Fig. 6). By correlating the **CT-fu/CNSL-fu** concentrations with the T_g of their respective polymers (Fig. 6), it was observed that the higher the **CT-fu** insertion, higher the T_g of the polymers (Fig. 7).

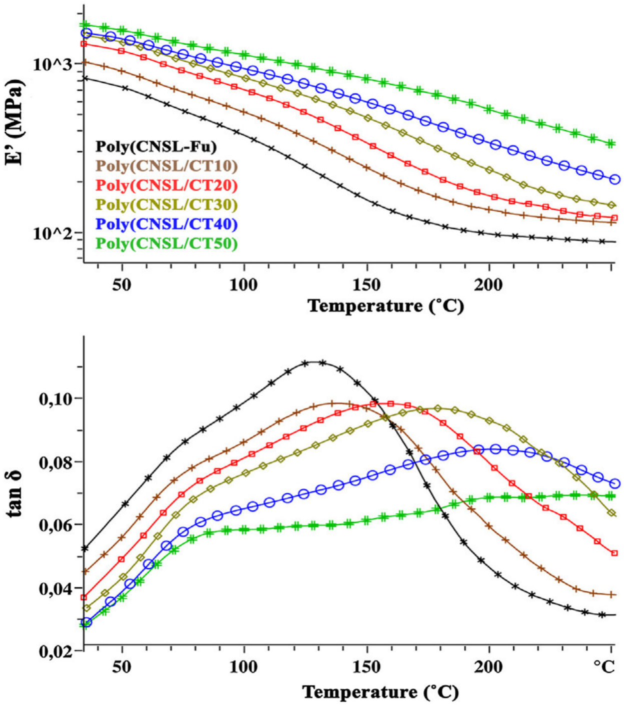


Fig. 6. DMA analyses of CT-fu/CNSL-fu copolymers.

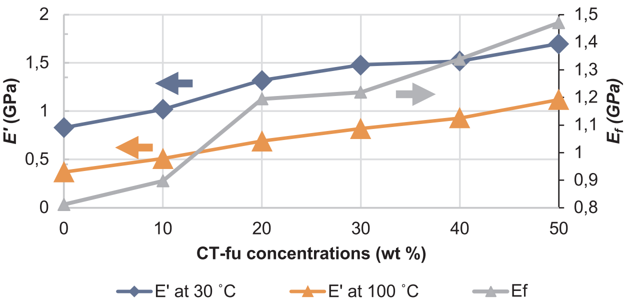


Fig. 7. Correlation of CT-fu/CNSL-fu concentration with *E'*

The glass transition temperature of **Poly(CNSL-fu)** was 129 °C, which is higher than the other cardanol-based polybenzoxazines that range from 85 to 106 °C [23,25]. By adding **CT-fu** content in the polymer, it was demonstrated that **Poly(CNSL/CT20)** had a similar T_g of **Poly(BA-a)**, which is 158 °C [43]. With further addition of **CT-fu** in the polymer composition, it was possible to reach T_g above 200 °C, as shown by **Poly(CNSL/CT40)**. The glass transition temperature of **Poly (CNSL/CT50)** could not be determined accurately, as no clear *α*-transition was observed. Even so, due to the linear increase tendency of **CT-fu** concentration from 10 to 40% with the T_g of their respective polybenzoxazines, it can be estimated that **Poly(CNSL/CT50)** had glass transition temperature above 250 °C.

Other relaxation activities were observed in the temperature range of 50–100 °C (Fig. 6), which is considered as *β*-transitions [49], probably associated with pendant group movements [50]. These specific relaxations could be associated mainly by the mobility of aliphatic chains from cardanol and cardol.

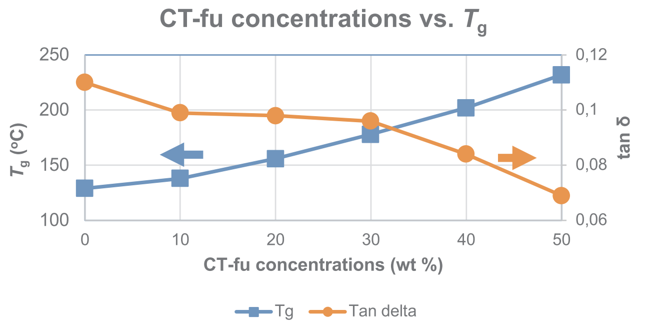


Fig. 8. Correlation of CT-fu/CNSL-fu concentration with α transitions of the (co)polybenzoxazines.

The stiffness, determined by the maximum tan *δ* value of the *α*-transition, of the polymers was also analyzed. The lower the tan *δ* value, higher the stiffness of the polymer. It was observed that the polymers had tan *δ* values varying between 0.08 and 0.11 (Fig. 8). The higher the **CT-fu** content, higher the stiffness of the polymer, which is expected since this monomer is composed mainly of aromatic groups. As it was not possible to observe an *α*-transition of **Poly(CNSL/CT50)**, its maximum tan *δ* value was not defined. Even so, the fact that the tan *δ* value of this polymer did not reach a tan *δ* value higher than 0.08 indicate that **Poly(CNSL/CT50)** possesses a very high stiffness.

The cross-linking density (ρ_x) of the each polybenzoxazine was also determined by using the storage modulus at the rubbery plateau (E_e') in Eq. (1) proposed by Nielsen [51].

$$Log(E'_e/3) = 7 + 293\rho_x \tag{1}$$

It was observed that as the **CT-fu** content increased in the polymer matrix, the higher cross-linking density, which was expected as bis-benzoxazine provides higher cross-linking than mono-benzoxazines. It was not possible to determine the cross-linking density of **Poly(CNSL/CT40)** and **Poly(CNSL/CT50)** as their respective storage modulus curves didn't reach the rubbery plateau till 250 °C.

Comparing the thermal properties of the polymers of the renewable resins of this work with the bisphenol A-based (**BA-a)** and other bio-based benzoxazine resins (Table 6), it was concluded that the fully bio-based **CNSL-fu/CT-fu** resins are very promising.

The polybenzoxazines containing 20–50% of **CT-fu** had similar or higher T_g and T_5 than of the commercial available **BA-a** and **Poly (CNSL/CT40)** and **Poly(CNSL/CT50)** had higher thermal stability than **Poly(BA-a)** as it can be observed by their *CY's*. This possibility to mix the **CNSL-fu** with **CT-fu** in different ratios can be seen as an advantage, since the thermal and mechanical properties of the polymers can easily be tuned for a desired application.

Other high-performance bi-functional bio-based benzoxazines, such as **C-pPDA**, **H-Fa** and **R-Fa**, demonstrated similar or higher thermal and thermo-mechanical properties than the **CNSL-fu/CT-fu** resins (Table 7). Unfortunately, the synthesis of these benzoxazines has one drawback. Their renewable starting materials, disregarding furfurylamine, are not

Table 6
Thermo-mechanical properties of polybenzoxazines obtained by DMA analyses.

Polymer	*E'* at 30 °C (GPa)	*E'* at 100 °C (GPa)	T_g (°C)	tan *δ*	ρx (0.10^{-3} mol/cm^3)
Poly(CNSL-fu)	0.83	0.37	129	0.110	4.98
Poly(CNSL/CT10)	1.02	0.51	138	0.099	5.34
Poly(CNSL/CT20)	1.32	0.69	156	0.098	5.48
Poly(CNSL/CT30)	1.48	0.82	178	0.096	5.72
Poly(CNSL/CT40)	1.52	0.93	202	0.084	N/D
Poly(CNSL/CT50)	1.70	1.12	> 250	< 0.07	N/D

Table 7
Comparison of thermal properties of catechol- and CNSL-based polybenzoxazines with reported (bio-based) polybenzoxazines.

Polybenzoxazines	T_g (°C)	T_5 (°C)	*CY* at 800 °C (%)
Poly(CNSL/CT20)	156	374	15
Poly(CNSL/CT30)	178	374	24
Poly(CNSL/CT40)	202	370	32
Poly(CNSL/CT50)	> 250	364	40
Poly(BA-a) [45] (BPA and Aniline)	156–157	279	30
C-pPDA [52]	~ 220*	–	–
(Chavicol and 1,4-diaminobenzene)	350**	413	~ 45
p(R-Fa) [27] (Resorcinol and furfurylamine)	270	335	~ 65
p(H-Fa) [27] (Hydroquinone and furfurylamine)	230	310	~ 65
U-da [53] (Urushiol and DDM)	135	350	25

* Cured at 250 °C.
** Cured at 300 °C.

commercially and widely available as CNSL and catechol.

4. Conclusion

Cashew Nutshell Liquid (**CNSL**) and lignocellulose are interesting renewable starting materials for large scale production of bio-based high-performance thermosetting resins as they are inexpensive and widely available. In this work **CNSL**, catechol and furfurylamine proved to be potential starting materials for the sustainable production of high-performance bio-based benzoxazine resins, **CNSL-fu** and **CT-fu**, since efficient eco-friendly methods were employed as determined by the sustainable metrics, *E*-factor and Atom Economy. As the liquid CNSL-based benzoxazine resins provide usually polybenzoxazines with low thermomechanical properties and the solid **CT-fu** possess poor processability issues, one resin can be used as a complement with the other, reaching copolymers with increased mechanical properties, highly stable thermal properties, glass transition temperatures above 200 °C and good flame retardancies. As the results demonstrate, these bio-based benzoxazine resins are interesting competitors against the BPA-based benzoxazine and other fossil-based thermosetting resins.

Acknowledgement

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Data availability

The raw/processed data required to reproduce these findings cannot be shared at this time as the data also forms part of an ongoing study.

Appendix A. Supplementary material

Supplementary data to this article can be found online at https://doi.org/10.1016/j.eurpolymj.2019.04.014.

References

[1] S.K. Bobade, N.R. Paluvai, S. Mohanty, S.K. Nayak, Bio-based thermosetting resins for future generation: a review, Polym. Plast. Technol. Eng. 55 (2016) 1863–1896, https://doi.org/10.1080/03602559.2016.1185624.

[2] B. Li, Y. Wang, N. Mahmood, Z. Yuan, J. Schmidt, C. (Charles) Xu, Preparation of bio-based phenol formaldehyde foams using depolymerized hydrolysis lignin, Ind. Crops Prod. 97 (2017) 409–416, https://doi.org/10.1016/j.indcrop.2016.12.063.

[3] M. Natarajan, S.C. Murugavel, Synthesis, spectral and thermal degradation kinetics of novolac resins derived from cardanol, High Perform. Polym. 25 (2013) 685–696, https://doi.org/10.1177/0954008313482955.

[4] V. Somisetti, S. Allauddin, R. Narayan, K.V.S.N. Raju, Flexible, hard, and tough biobased polyurethane thermosets from renewable materials: glycerol and 10-undecenoic acid, J. Coatings Technol. Res. 15 (2018) 199–210, https://doi.org/10.1007/s11998-017-9998-2.

[5] S. Sahoo, S. Mohanty, S.K. Nayak, Biobased polyurethane adhesive over petroleum based adhesive: use of renewable resource, J. Macromol. Sci. Part A. 55 (2018) 36–48, https://doi.org/10.1080/10601325.2017.1387486.

[6] M. Kathalewar, A. Sabnis, D. D'Melo, Polyurethane coatings prepared from CNSL based polyols: synthesis, characterization and properties, Prog. Org. Coatings. 77 (2014) 616–626, https://doi.org/10.1016/j.porgcoat.2013.11.028.

[7] F. Ng, G. Couture, C. Philippe, B. Boutevin, S. Caillol, Bio-based aromatic epoxy monomers for thermoset materials, Molecules 22 (2017) 149, https://doi.org/10.3390/molecules22010149.

[8] Y. Yagci, B. Kiskan, N.N. Ghosh, Recent advancement on polybenzoxazine – a newly developed high performance thermoset, J. Polym. Sci. Part A Polym. Chem. 47 (2009) 5565–5576, https://doi.org/10.1002/pola.23597.

[9] P. Froimowicz, K. Zhang, H. Ishida, Intramolecular hydrogen bonding in benzoxazines: when structural design becomes functional, Chem. – A Eur. J. 22 (2016) 2691–2707, https://doi.org/10.1002/chem.201503477.

[10] L. Dumas, L. Bonnaud, M. Olivier, M. Poorteman, P. Dubois, Arbutin-based benzoxazine: en route to an intrinsic water soluble biobased resin, Green Chem. 18 (2016) 4954–4960, https://doi.org/10.1039/C6GC01229A.

[11] H. Ishida, T. Agag, Handbook of Benzoxazine Resins, in: H. Ishida, T. Agag (Eds.), Handb. Benzoxazine Resins, Elsevier, Oxford, 2011. p. 712.

[12] D. Lomonaco, F.J.N. Maia, C.S. Clemente, J.P.F. Mota, A.E. Costa, S.E. Mazzetto, Thermal studies of new biodiesel antioxidants synthesized from a natural occurring phenolic lipid, Fuel 97 (2012) 552–559, https://doi.org/10.1016/j.fuel.2012.01.059.

[13] S.E. Mazzetto, D. Lomonaco, Cashew nut oil: opportunities and challenges in the context of sustainable industrial, Quim. Nova. 32 (2009) 732–741.

[14] FAO, FAO; 2018 < http://faostat3.fao.org/faostat-gateway/go/to/browse/Q/QC/E > (accessed September 28, 2018).

[15] L.R.V. Kotzebue, F.W.M. Ribeiro, V.G. Sombra, J.P.A. Feitosa, G. Mele, S.E. Mazzetto, D. Lomonaco, Spectral and thermal studies on the synthesis and catalyzed oligomerization of novel cardanol-based benzoxazines, Polymer 92 (2016) 189–200, https://doi.org/10.1016/j.polymer.2016.04.005.

[16] D. Lomonaco, G. Mele, S.E. Mazzetto, Cashew Nutshell Liquid (CNSL): From an Agro-industrial Waste to a Sustainable Alternative to Petrochemical Resources, in: P. Anilkumar (Ed.), Cashew Nut Shell Liq., Springer, Cham, Zurich, 2017: pp. 19–38. 10.1007/978-3-319-47455-7_2.

[17] S. Laurichesse, L. Avérous, Chemical modification of lignins: towards biobased polymers, Prog. Polym. Sci. 39 (2014) 1266–1290, https://doi.org/10.1016/j.progpolymsci.2013.11.004.

[18] R. Ma, M. Guo, X. Zhang, Recent advances in oxidative valorization of lignin, Catal. Today 302 (2018) 50–60, https://doi.org/10.1016/j.cattod.2017.05.101.

[19] X. Erdocia, R. Prado, M.Á. Corcuera, J. Labidi, Base catalyzed depolymerization of lignin: influence of organosolv lignin nature, Biomass Bioenergy 66 (2014) 379–386, https://doi.org/10.1016/j.biombioe.2014.03.021.

[20] S. Jeenpadiphat, I. Mongkolpichayarak, D.N. Tungasmita, Catechol production from lignin by Al-doped mesoporous silica catalytic cracking, J. Anal. Appl. Pyrolysis. 121 (2016) 318–328, https://doi.org/10.1016/j.jaap.2016.08.011.

[21] J. Fernández-Rodríguez, X. Erdocia, C. Sánchez, M. González Alriols, J. Labidi, Lignin depolymerization for phenolic monomers production by sustainable processes, J. Energy Chem. 26 (2017) 622–631, https://doi.org/10.1016/j.jechem.2017.02.007.

[22] L.R.V. Kotzebue, J.R. de Oliveira, J.B. da Silva, S.E. Mazzetto, H. Ishida, D. Lomonaco, Development of fully biobased high-performance bis-benzoxazine under environmentally friendly conditions, ACS Sustain. Chem. Eng. 6 (2018) 5485–5494, https://doi.org/10.1021/acssuschemeng.8b00340.

[23] F.W.M. Ribeiro, L.R.V. Kotzebue, J.R. Oliveira, F.J.N. Maia, S.E. Mazzetto, D. Lomonaco, Thermal and mechanical analyses of biocomposites from cardanol-based polybenzoxazine and bamboo fibers, J. Therm. Anal. Calorim. 129 (2017) 281–289, https://doi.org/10.1007/s10973-017-6191-x.

[24] S. Shukla, A. Mahata, B. Pathak, B. Lochab, Cardanol benzoxazines – interplay of oxazine functionality (mono to tetra) and properties, RSC Adv. 5 (2015) 78071–78080, https://doi.org/10.1039/C5RA14214H.

[25] R. Ambrožič, U. Šebenik, M. Krajnc, Synthesis, curing kinetics, thermal and mechanical behavior of novel cardanol-based benzoxazines, Polymer 76 (2015) 203–212, https://doi.org/10.1016/j.polymer.2015.08.065.

[26] C. Wang, C. Zhao, J. Sun, S. Huang, X. Liu, T. Endo, Synthesis and thermal properties of a bio-based polybenzoxazine with curing promoter, J. Polym. Sci. Part A Polym. Chem. 51 (2013) 2016–2023, https://doi.org/10.1002/pola.26587.

[27] L. Dumas, L. Bonnaud, M. Olivier, M. Poorteman, P. Dubois, High performance bio-based benzoxazine networks from resorcinol and hydroquinone, Eur. Polym. J. 75 (2016) 486–494, https://doi.org/10.1016/j.eurpolymj.2016.01.021.

[28] O.A. Attanasi, M.S. Behalo, G. Favi, D. Lomonaco, S.E. Mazzetto, G. Mele, I. Pio, G. Vasapollo, Solvent free synthesis of novel mono- and bis-benzoxazines from cashew nut shell liquid components, Curr. Org. Chem. 16 (2012) 2613–2621, https://doi.org/10.2174/138527212804004616.

[29] C. Voirin, S. Caillol, N.V. Sadavarte, B.V. Tawade, B. Boutevin, P.P. Wadgaonkar,

Functionalization of cardanol: towards biobased polymers and additives, Polym. Chem. 5 (2014) 3142–3162, https://doi.org/10.1039/C3PY01194A.

[30] F.H. Isikgor, C.R. Becer, Lignocellulosic biomass: a sustainable platform for the production of bio-based chemicals and polymers, Polym. Chem. 6 (2015) 4497–4559, https://doi.org/10.1039/C5PY00263J.

[31] R.A. Sheldon, The road to biorenewables: carbohydrates to commodity chemicals, ACS Sustain. Chem. Eng. 6 (2018) 4464–4480, https://doi.org/10.1021/acssuschemeng.8b00376.

[32] M.J. Hülsey, H. Yang, N. Yan, Sustainable routes for the synthesis of renewable heteroatom-containing chemicals, ACS Sustain. Chem. Eng. 6 (2018) 5694–5707, https://doi.org/10.1021/acssuschemeng.8b00612.

[33] J.R. Oliveira, L.R.V. Kotzebue, F.W.M. Ribeiro, B.C. Mota, D. Zampieri, S.E. Mazzetto, H. Ishida, D. Lomonaco, 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. Part A Polym. Chem. 55 (2017) 3534–3544, https://doi.org/10.1002/pola.28755.

[34] A.M. Rodríguez, P. Prieto, A. de la Hoz, Á. Díaz-Ortiz, D.R. Martín, J.I. García, Influence of polarity and activation energy in microwave-assisted organic synthesis (MAOS), ChemistryOpen. 4 (2015) 308–317, https://doi.org/10.1002/open.201402123.

[35] Y.-L. Liu, C.-I. Chou, High performance benzoxazine monomers and polymers containing furan groups, J. Polym. Sci. Part A Polym. Chem. 43 (2005) 5267–5282, https://doi.org/10.1002/pola.21023.

[36] L. Han, D. Iguchi, P. Gil, T.R. Heyl, V.M. Sedwick, C.R. Arza, S. Ohashi, D.J. Lacks, H. Ishida, Oxazine ring-related vibrational modes of benzoxazine monomers using fully aromatically substituted, deuterated, 15 N isotope exchanged, and oxazine-ring-substituted compounds and theoretical calculations, J. Phys. Chem. A. 121 (2017) 6269–6282, https://doi.org/10.1021/acs.jpca.7b05249.

[37] R.A. Sheldon, Metrics of green chemistry and sustainability: past, present, and future, ACS Sustain. Chem. Eng. 6 (2018) 32–48, https://doi.org/10.1021/acssuschemeng.7b03505.

[38] P.T. Anastas, J.C. Warner, Green Chemistry: Theory and Practice, Oxford University Press, New York, 1998 http://www.epa.gov/gcc/pubs/principles.html.

[39] B.M. Trost, The atom economy–a search for synthetic efficiency, Science 254 (5037) (1991) 1471–1477, https://doi.org/10.1126/science:1962206.

[40] R.A. Sheldon, Organic synthesis – past, present and future, Chem. Ind. (1992) 903–906.

[41] L. Dumas, L. Bonnaud, M. Olivier, M. Poorteman, P. Dubois, Bio-based high performance thermosets: stabilization and reinforcement of eugenol-based benzoxazine networks with BMI and CNT, Eur. Polym. J. 67 (2015) 494–502, https://doi.org/10.1016/j.eurpolymj.2014.11.030.

[42] B. Lochab, I.K. Varma, J. Bijwe, Thermal behaviour of cardanol-based benzoxazines, J. Therm. Anal. Calorim. 102 (2010) 769–774, https://doi.org/10.1007/s10973-010-0736-6.

[43] Huntsman, Benzoxazines, 2018. http://www.huntsman.com/advanced_materials/a/Our Technologies/High Performance Components/Imides and Benzoxazines/Benzoxazines (accessed September 22, 2018).

[44] H. Ishida, D.P. Sanders, Improved thermal and mechanical properties of polybenzoxazines based on alkyl-substituted aromatic amines, Polymer 38 (2000) 3289–3301, https://doi.org/10.1002/1099-0488(20001215)38.

[45] S. Kopsidas, I. Hamerton, Examining the thermal behaviour of novel aromatic polybenzoxazine blends containing an organophosphorous compound and polyhedral oligomeric silsesquioxane reagents, Polym. Int. 65 (2016) 1015–1023, https://doi.org/10.1002/pi.5139.

[46] A.Q. Dayo, B. Gao, J. Wang, W. Liu, M. Derradji, A.H. Shah, A.A. Babar, Natural hemp fiber reinforced polybenzoxazine composites: curing behavior, mechanical and thermal properties, Compos. Sci. Technol. 144 (2017) 114–124, https://doi.org/10.1016/j.compscitech.2017.03.024.

[47] D. van Krevelen, Some basic aspects of flame resistance of polymeric materials, Polymer 16 (1975) 615–620, https://doi.org/10.1016/0032-3861(75)90157-3.

[48] S. Mallakpour, A. Zadehnazari, Improved covalent functionalization of multi-walled carbon nanotubes using ascorbic acid for poly(amide–imide) composites having dopamine linkages, Bull. Mater. Sci. 40 (2017) 213–222, https://doi.org/10.1007/s12034-017-1358-4.

[49] X. Ning, H. Ishida, Phenolic materials via ring-opening polymerization of benzoxazines: effect of molecular structure on mechanical and dynamic mechanical properties, J. Polym. Sci. Part B Polym. Phys. 32 (1994) 921–927, https://doi.org/10.1002/polb.1994.090320515.

[50] K.P. Menard, Dynamic Mechanical Analysis – A Practical Introduction, in: CRC Press, Boca Raton, 1999. p. 240.

[51] L.E. Nielsen, Cross-linking–effect on physical properties of polymers, J. Macromol. Sci. Part C. 3 (1969) 69–103, https://doi.org/10.1080/15583726908545897.

[52] L. Dumas, L. Bonnaud, M. Olivier, M. Poorteman, P. Dubois, Chavicol benzoxazine: ultrahigh Tg biobased thermoset with tunable extended network, Eur. Polym. J. 81 (2016) 337–346, https://doi.org/10.1016/j.eurpolymj.2016.06.018.

[53] H. Xu, W. Zhang, Z. Lu, G. Zhang, Hybrid polybenzoxazine with tunable properties, RSC Adv. 3 (2013) 3677, https://doi.org/10.1039/c3ra22247k.