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Graphical Abstract
47x21mm (600 x 600 DPI)

MINIREVIEW

Polybenzoxazines: New Players in the Bio-Based Polymers Arena

**Gerard Lligadas,* Alev Tüzün, Juan C. Ronda, Marina Galià, Virginia Cádiz**

Polybenzoxazines are phenolic-like materials that have attracted significant attention of both academia and industry because of their unique advantages. The growth of this technology has always been linked to petro-based feedstocks. However, due to the incessant global energy crisis it is now finding a breakthrough through the preparation of their monomers from renewable resources. This mini-review focuses on the recent efforts to replace petro-based feedstocks from polybenzoxazine precursors.

Introduction

In recent years, the choice of raw materials for chemical purposes has been a key subject of interest to researchers due strong environmental incentives to reduce consumption of petroleum and its derivatives. In this context, polymer researchers are devoting increasing attention on the utilization of renewable resources as raw materials for the production of the majority of synthetic polymer building blocks.[1,2] The interest in bio-based polymers is not merely academic as evidenced by the fact that some polymers with high renewable content are already on the market. Rilsan®, a polyamine based on castor oil, sugar-derived polyesters such as Sorona® and Hytrel®, and the Pearlthane® ECO thermoplastic polyurethane ranges marketed by Merquinsa are successful examples. Polybenzoxazines are by no means an exception and have recently become new players in the bio-based polymers arena.

Polybenzoxazines are a relatively new class of polymeric phenolic resins having various outstanding characteristics, including minimal moisture absorption, good thermal stability, high char yield, high glass transition temperature, and no harsh catalyst required, no volatile release and near-zero volume changes during cure.[3] The polymerization of 1,3-benzoxazines takes place through thermally activated ring opening of the cyclic benzoxazine structure, in the absence of a catalyst or initiator and without generating any by-products, and produces polymers comprised of a phenol and tertiary amine bridge as the structural motif.

Their monomers, 1,3-benzoxaines are typically generated by the Mannich-like condensation of commercially available and inexpensive phenols, amines, and formaldehyde, offering an extraordinary monomer design flexibility (Scheme 1).[4,5] To date, the developments of this technology have focused on overcome benzoxazine chemistry shortcomings while retaining their benefits. Thus, for example, high temperature needed for complete curing or brittleness of the cured materials are problems that have been addressed by synthesizing benzoxazine monomers with additional functionality or incorporating benzoxazine reactive groups into polymeric chains respectively.[3,6]
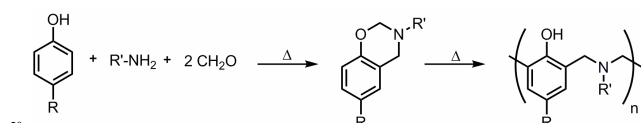

Scheme 1 Classical benzoxazine monomer synthesis and thermal polymerization
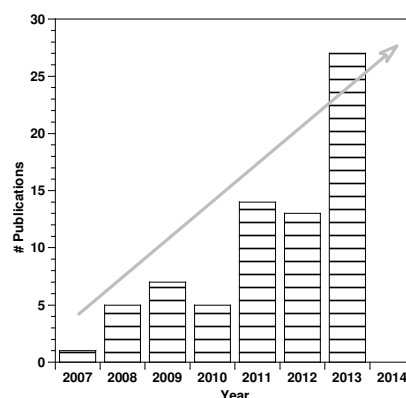
Figure 1 Number of publications involving benzoxazines and renewable resources since 2007 (Scopus, June 2014)

However, due to the alarming rate of depletion of petroleum-based products, polybenzoxazine technology is now finding a breakthrough through the preparation of their monomers from renewable resources in the same way as other petroleum-based polymers (Figure 1).[7] Taking into account that formaldehyde is within the area of influence of biomethanol, the two remaining benzoxazine building blocks, phenols and amines, are right now in the spotlight. Although the first attempt to incorporate natural components to benzoxazine-based materials dates from 1999,[8] it was not until recently when both academia and industry have focused their efforts to exploit renewable resources, paying special attention to naturally occurring phenolics and other bio-based phenols. Renewable amines have otherwise received limited attention probably due to its lower natural stock. A facile and efficient benzoxazine monomer synthesis protocol combined with the characteristic structural wealth of these natural compounds offers a palette of possibilities to design polybenzoxazine precursors with comparable and in some cases superior properties than well-studied petroleum-based polybenzoxazines. The purpose of this mini-review is to comprehensively overview recent efforts for either partial or complete replacement of petro-based feedstocks from polybenzoxazine precursors.
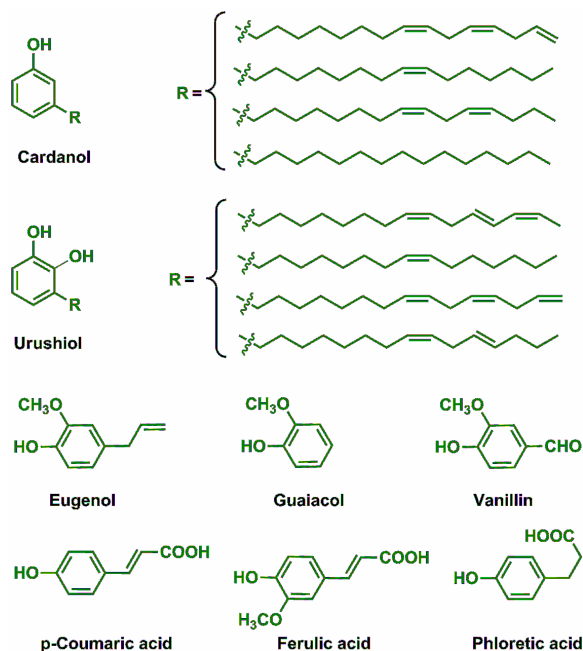
Scheme 2 Chemical structure of plant-derived phenolics used as benzoxazine monomers precursors. Only the most abundant side alkyl chains are shown in R.

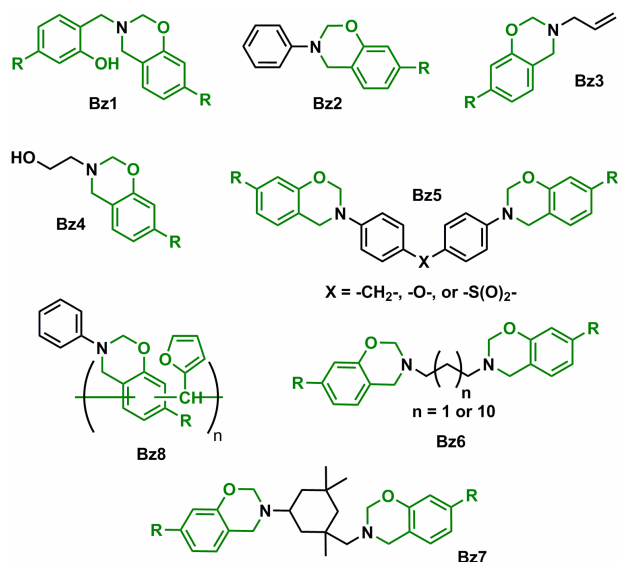**Scheme 3** Chemical structure of cardanol and cardanol-based mono- and bis-benzoxazines.

Plant-derived Phenolics as Platform Chemicals for Benzoxazine Technology

Phenolics are broadly distributed in the plant kingdom and are the most abundant secondary metabolites in plants.[9] They exist with an incredible diversity of several thousands of structures ranging from simple single-ring molecules with, for example, C_6, C_6-C_1, or C_6-C_3 basic skeleton to highly polymerized substrates. Biogenetically, these compounds arise from two main pathways: the shikimate pathway, which directly provides phenylpropanoids such as hydroxycinnamic acids and coumarins, and the polyketide (acetate) pathway, which can produce simple phenols and also lead to quinones. The flavonoids, by far the largest group of phenolics, are derived by combination of these two pathways.

The fact that natural phenolics are found in large amounts either in natural existing plant sources or wastes generated from agro-based industries makes them potential substitutes for phenolic petrochemicals. However, it is important to point out that only abundant and easily isolable phenolics are economically feasible. In this context, the incorporation of abundant plant-derived phenolics into benzoxazine building blocks has been considered the simple and straightforward approach to reduce benzoxazine chemistry reliance on petroleum. Monomeric phenols derived from lignocellulosic biomass have also been considered. Chemical structures of all plant derived phenolics exploited for such purposes are shown in Scheme 2.

Benzoxazine Monomers from Naturally Occurring Phenolics

Cardanol, urushiol, and eugenol are three naturally occurring single-ring phenols that have been used as building blocks of benzoxazine monomers. Cardanol and urushiol belong to the phenolic lipids class of chemical compounds composed of a long hydrophobic alkyl chain linked to a phenolic ring, whereas eugenol is a member of the C_6-C_3 phenylpropanoids, synthesized by plants from te amino acid phenyalanine via shikimate pathway. Urushiol and eugenol can be considered abundant naturally occurring phenols because exist in high percentage in the sap of Chinese and Japanese lacquer tree (60-65%)[10,11] and the essential oil extracted from cloves (72-90%), respectively. Although cardanol is also considered a sustainable and largely available natural resource, its case is quite special. In fact, cardanol is naturally found in cashew nut shell liquid (CNSL), a byproduct of the cashew nut industry. However, natural CNSL contains other three components: anacardic acid, cardol, and 2-methyl cardol, being anacardic acid the main component (~75%). Nevertheless, cardanol is the main component of commercial grade CNSL because anacardic acid descarboxylates to cardanol during the roasting process used industrially to extract the oil from cashew nuts.

Clearly, cardanol is the most widely exploited plant-derived phenol for bio-based benzoxazine synthesis purposes. The literature reports several examples of cardanol-based benzoxazines (Scheme 3 where biobased part is highlighted in green). The pioneer work, reported by Mele and coworkers, described the preparation of the benzoxazine Bz1 using cardanol, ammonia and formaldehyde as starting materials.[12] Interestingly, Bz1 contains two molecules of cardanol per oxazine unit, leading to a monomer with high biobased content value. Differential scanning calorimetric (DSC) analysis of Bz1 showed a exothermic peak associated with curing from 160ºC to 275ºC with a peak maximum of 243ºC. Compared to, for example, phenol/aniline benzoxazine monomer, the curing of Bz1 takes place at much lower temperature. This lowering of cure temperature is due to catalysis of phenolic group as reported in the literature.[13] Cardanol has also combined with other amines such as aniline[14,15,16,17] (Bz2, Scheme 2), allylamine[18] (Bz3), ethanolamine (Bz4) and a series of aromatic[19,20] and aliphatic diamines[21] such as 4,4'-diaminodiphenylmethane (DDM) (Bz5 with X = -CH₂-) and isophorone diamine (Bz7) to yield different benzoxazines with a broad range of applications. Additionally, cardanol-furfural phenolic resins were also used to prepare oligomeric benzoxazine precursors (Bz8).[22] Furfural is also green platform product derived from a variety of agricultural by-producs such as corncorbs and wheat bran.

In comparison with classical systems, most of cardanol-derived benzoxazines are liquid monomers with low viscosity at room temperature. This characteristic feature has been
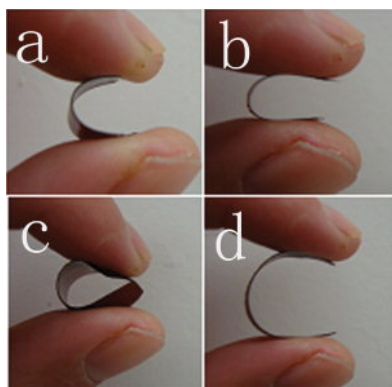
Figure 2 Photographs of the bending for a) polybenzoxazine Bz4 and polybenzoxazine/SiO$_2$ hybrids with Bz4:TEOS (w/w) ratios b) 5:1, c) 5:3, and d) 5:5. Reproduced from Ref. [24] with permission from Wiley-VCH.

exploited technologically to develop cardanol-based benzoxazine reactive diluents for petroleum-based epoxy and benzoxazine resins. For example, Gu et al. recently demonstrated that Bz5 bis-benzoxazines containing different bridging groups are able to significantly reduce the melting viscosity of DDM/phenol-based bisbenzoxazine and improve the toughness of the copolymers due to the plasticizing effect and flexibility of their alkyl side chains.[19] Some cardanol-derived benzoxazines have also shown good performance as thermosetting matrix for natural fiber-reinforced composites and organic-inorganic hybrid materials.[12,16,18,23] For example, Li et al. successfully synthesized Bz4-based polybenzoxazine/SiO$_2$ hybrids by the sol-gel procedure.[24] The preparation of the hybrids mainly included the hydrolysis and the following condensation of tetraethoxysilane (TEOS) at room temperature, further condensation reactions of silanol groups and the ring-opening reaction of benzoxazine moieties at high temperature. As can be seen in Figure 2, flexibility of films improved for 5:1 and 5:3 Bz4:TEOS (w/w) content. Dewetting and UV resistance properties also improved with silicon content.

Similarly to cardanol, urushiol-based mono- and bis-benzoxazine monomers and derived polymers showed properties dominated by the presence of the hydroxyl group and the alkyl side chain that remain in the benzoxazine structure (Figure 3). Thus, for example, Bz8, prepared via condensation reaction of urushiol, aniline, and paraformaldehyde in dioxane, was isolated as a liquid and showed relatively low curing temperature curing (180ºC) without addition of catalyst.[25] Moreover it produced polybenzoxazine with low T$_g$, superb toughness and extraordinary elongation at break.

In this case it is important to point out that FTIR analysis of the curing process showed that oxazine polymerization takes place simultaneously with crosslinking of olefins in the side chains yielding a highly crosslinked polymer. Futhermore, the bis-benzoxazine Bz9 and DDM/phenol bis-benzoxazine were copolymerized into hybrid polybenzoxazines, where the alkyl chains in Bz9 improved the ductility of the materials.[26] As can be seen in Figure 3B, as the the Bz9 content increases, the elongation at break increases and the stress at break decreases.

Eugenol has only been considered in the preparation of bis-benzoxazines. A series of eugenol-derived monomers (Bz10-13, Figure 4A) were prepared from various aromatic diamines and paraformaldehyde.[27]
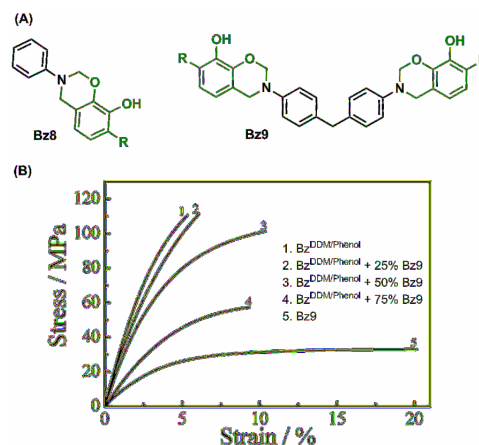

Figure 3 (A) Chemical structure of urushiol-based mono- and bis-benzoxazine, and (B) Stress-strain curves for Bz9 and DDM/phenol polybenzoxazine copolymers. Partially reproduced from Ref. 26 with permission from The Royal Society of Chemistry.
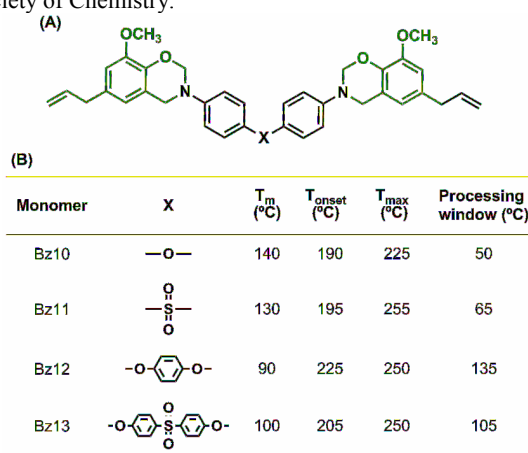

Monomer	X	T$_m$ (ºC)	T$_{onset}$ (ºC)	T$_{max}$ (ºC)	Processing window (ºC)
Bz10	—O—	140	190	225	50
Bz11	—S— (O/O)	130	195	255	65
Bz12	-O-⬡-O-	90	225	250	135
Bz13	-O-⬡-S-⬡-O- (O/O)	100	205	250	105

Figure 4 (A) Chemical structures and (B) DSC data of eugenol-based bis-benzoxazines.

As summarized in Figure 4B, Bz10-13 were isolated as powders with high melting temperatures at around 100ºC. Interestingly, Bz12 and Bz13 showed wider processing window, defined as the temperature difference between the melting point and onset of polymerization, indicating better processability. FTIR data support that Bz10-13 shows similar curing behaviour than urushiol-derived systems, with allyl moieties also participating during the curing process. Polybenzoxazines prepared by heating up monomers Bz10-13 to 250ºC, to ensure benzoxazine and allyl groups crosslinking, produced materials with T$_g$ values ranging from 120 to 155ºC although flexible ether and sulfone linkages in Bz10 and Bz11 produced lower T$_g$ materials. In all cases, polymers with high char yield in the range of 23-36% at 800ºC in N$_2$ and good flame retardance in terms of their LOI values were obtained.

Benzoxazine Monomers from Lignin-derived Phenols

Lignocellulosic materials, which can be found in either the natural existing plant sources or wastes generated from agro-based industries, are one of the most attractive biomass resources in nature and therefore have not gone unnoticed by benzoxazine researchers. Lignocellulosic biomass is composed of cellulose (40-50%), hemicellulose (20-40%) and lignin (20-30%).[28] Proteins, oils and ash make up the remaining fraction. Cellulose and hemicellulose are polysaccharides whereas lignin
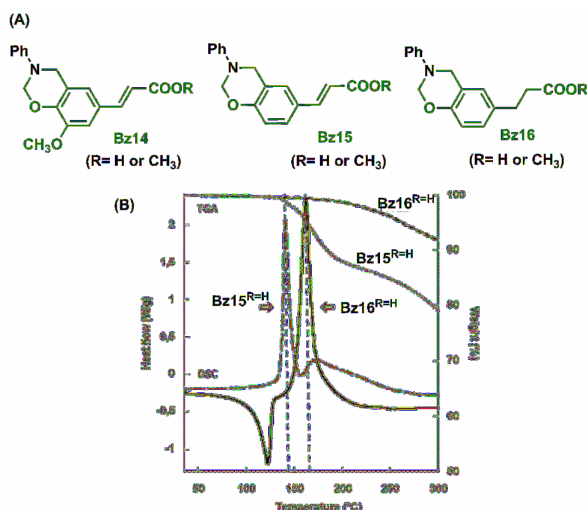
Figure 5 (A) Chemical structures of benzoxazine monomers based on ferulic, p-coumaric, and phloretic acids and their corresponding esters. (B) DSC/TGA curves for Bz15 and Bz16 with R=H.
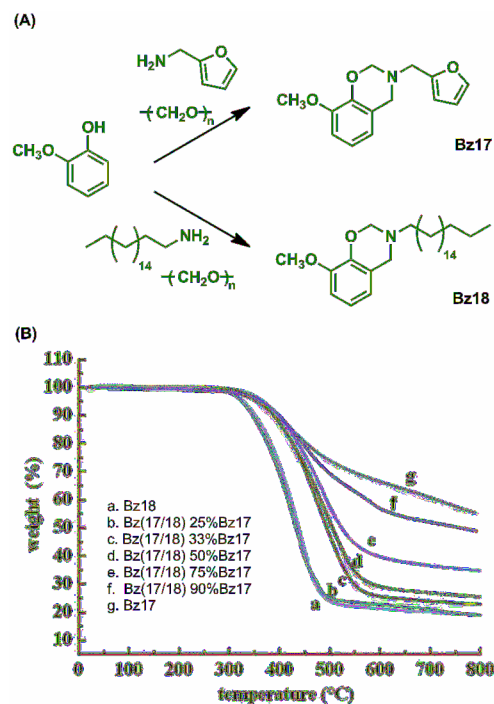
is a highly branched phenylpropanoid polymer framework assembled by oxidative coupling of p-coumaroyl alcohol, coniferyl alcohol and sinapoyl alcohol.[29] In recent years, conversion of lignocellulosic biomass to fuel and chemicals is globally gaining significant prominence.[30, 31]

Hydroxycinnamic acids, principally ferulic acid and *p*-coumaric acid (see Scheme 2), are abundant molecules in lignocellulose materials with the function to bind lignin to the hemicellulose and cellulose in plant cell walls. Although p-coumaric and ferulic acids are present in relatively large quantities in vegetables like peanuts, tomatoes, fennel, coffee, or artichokes, as main components of lignocellulose, they are commercially produced mainly by chemical or enzymatic transformation of corn, sugarcane, and other agricultural bagasses.[32-34] Our group recently investigated the preparation of polybenzoxazines based on p-coumaric, ferulic, and phloretic acids.[35] Phloretic acid can be obtained by hydrogenation of p-coumaric acid but it is commonly produced by chemical or enzymatic treatment of phloretin, a dihydrochalcone present in the apple tree leaves. Monomers Bz14-16 synthesis was carried out using 1,3,5-triphenylhexahydro-1,3,5-triazine and para-formaldehyde as reagents to minimize oligomers formation (Figure 5). Unfortunately, the high melting point of free acids prevented to use bulk conditions and toluene had to be added as solvent. In the case of methyl ester derivatives, reactions could be carried out in bulk with a significant shortening of the reaction time. Benzoxazines with conjugated unsaturated chains exhibited unusual poor thermal stability and partially degrade at the polymerization temperature making necessary the use of a $BF_3 \cdot Et_2O$ catalyst to low the polymerization temperature and prevent degradation. DSC and TGA curves (Figure 5B) show that for Bz15 thermal benzoxazine ring opening polymerization is overlapped with thermal decomposition of the monomer, which involves weight loss around 15% of the initial mass. A different behaviour was observed in Bz16 containing a saturated C3 substituient. In this way, only phloretic acid-based benzoxazines could be polymerized without catalyst. Polybenzoxazines from Bz14-16 and the corresponding methyl esters were obtained as hard and brittle materials with T_g values ranging from 120 to 150ºC. These high T_g values, compared to phenol/aniline benzoxazine, were attributed to the occurrence

Figure 6 (A) Synthesis of fully biobased guaiacol-derived benzoxazines Figure 4. (B) TGA thermograms of Bz17/Bz18 polybenzoxazine copolymers. Partially reproduced from Ref. 38 with permission from The Royal Society of Chemistry.
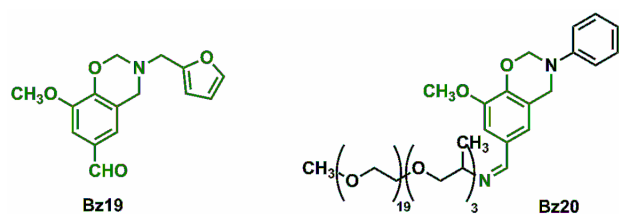
of addicional esterification and transesterification reactions between the phenolic hydroxyl groups resulting from the oxazine ring opening and the free carboxylic or methyl ester groups.

Lignin is a valuable source of chemicals, particularly phenols, when selectively depolymerised via pyrolysis, hydrogenolysis, hydrolysis or enzymatic disassembly reactions.[36,37] Guaiacol is a typical lignin breakdown product that has been recently used as phenolic building block to prepare benzoxazine monomers. Using a solventless synthesis procedure and starting materials entirely derived from biobased feedstocks, guaiacol was combined with furfurylamine and stearyl amine in the presence of paraformaldehyde to prepare benzoxazine monomers Bz17 and Bz18 (Figure 6A).[38] Furfurylamine has also been incorporated into other petroleum-based polybenzoxazine systems.[39,40] Industrially, furfurylamine is obtained from furfural. On the other hand, stearylamine can be produced from vegetable oils.

Bz17 and Bz18 were obtained in high yields as white solids with melting points at 97 and 59ºC, respectively. Homopolymerization of both monomers was investigated. Bz17 and Bz18 homopolymers exhibited Tg values of 150 and 93ºC, indicating that furfurylamine-based benzoxazine has higher crosslinking density and backbone rigidity. In fact, the furan moiety of Bz17 participates in ring-opening polymerization of benzoxazines via electrophilic aromatic substitution. Finally, both benzoxazines were copolymerized in order to improve the crosslinking density of the resins and therefore enhance properties such as Tg, thermal stability and char yield. Figure 6B shows a remarkable improvement of the char yields for the copolymers, with the char yields of all the copolymers exceeding that of the neat polybenzoxazine derived from Bz18. Furthermore, the addition of methyl p-toluensulfonate to Bz17 demonstrated to significantly improve its polymerization behaviour, producing a decrease in the

Scheme 4 Chemical structures of vanillin-based mono-benzoxazines.

5 polymerization temperature from 240 to 174ºC, a shortening of the time required to reach the gel point on heating at 200ºC from 47 to 20 min, and an increase in the char yield at 800ºC of the cured resin from 53 to 62%.[41]

Another renewable natural resource that can be obtained in 10 large quantities from lignin is vanillin.[42,43] Vanillin is of great interest for benzoxazine chemistry because contains an aldehyde group that is not expected to be consumed during benzoxazine synthesis. In fact, Varma et al. synthesized and characterized a renewable benzoxaine monomer from vanillin, 15 furfurylamine and paraformaldehyde using a solventless method (Bz19, Scheme 4).[44] Interestingly, DSC analysis of Bz19 shows a low temperature curing behaviour, showing a curing exotherm in the range of 179-232ºC with a maximum at 205ºC. This low curing temperature was attributed to the 20 oxidation of formyl group to carboxylic groups which catalyses the ring-opening polymerization of benzoxazines. On the other hand, Ishida et al. exploited the aldehyde group of vanillin/aniline benzoxazine to expand benzoxazine applications as surfactants.[45] The aldehyde of N-phenyl 25 vanillin-derived benzoxazine monomer was further reacted with amine terminated poly(ethylene oxide) to form a benzoxazine surfactant Bz20. Emulsification using Bz20 was successful in producing polystyrene particles of 627 nm in average diameter with a polydispersity of 1.24, determined by 30 dynamic light scattering. The miniemulsion was stable for up to 2 weeks without significant deposition.

Biobased Synthetic Phenols as Platform Chemicals for Benzoxazine Technology

The utilization of partially biobased phenols is an alternative 35 approach to incorporate natural components into benzoxazine monomers. Terpenediphenol (TPD) and maleopimaric acid imidophenol (MAI) are succesfull examples, although diphenolic acid (DPA) is the product that has received much attention (Scheme 5). TPD is one of the most important 40 derivative of terpenes, which are important natural compounds widely produced by various plants, typically conifers. TPD, synthesized from terpene compounds that are contained in pine or orange rind, and excess phenol has a rigid molecule structure of the aromatic and cyclohexane rings, thus TPD is expected to 45 be a monomer for high T_g and high dimensional stability bioplastics. With the aim to improve the mechanical and water resistance properties of benzoxazine/epoxy resins, 1,3- and 2,8-TPD-derived N-phenyl benzoxazine monomers were synthesized in 1,4-dioxane or tetrahydrofuran as a solvent from 50 a TPD mixture containing 2:1 ratio of both structural isomers.[8] 1,3- and 2,8-Bz21 were copolymerized with equimolar amounts of diglycidyl ether of bisphenol A (DGEBA), and the cured resins had superior heat resistance, electrical insulation and especially water resistance, compared with the cured resin from 55 bisphenol A (BPA) type novolac and epoxy resin. The percent of water absorption after boiling for 2h was improved from 0.54 wt-% for BPA benzoxazine/epoxy mixture to 0.28 wt-%
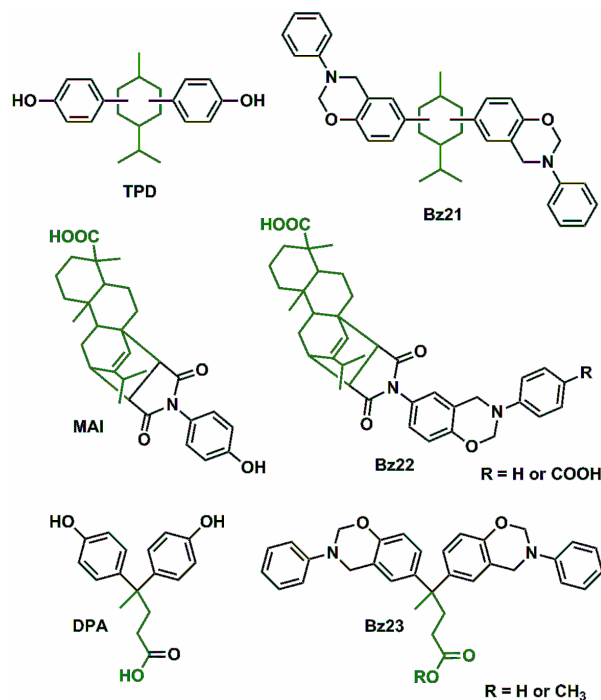
Scheme 5 Chemical structures of terpenediphenol (TPD), 60 maleopimaric acid imidophenol (MAI), and diphenolic acid (DPA) as well as their corresponding N-phenyl benzoxazies.

for 2,8-Bz21/DGEBA resin. In fact, the polybenzoxazine rigidity, inferred by the inclusion of the TPD rigid hydrocarbon 65 ring into the network structure, contributes to decrease water absorption. MAI is another rigid structure that has been used as partially biobased phenolic component in benzoxazine monomers (Bz22, Scheme 7).[46] MAI was obtained from rosin, which is a versatile natural mixture of unsaturated polycyclic 70 carboxylic acids, especially abietic acid, obtained from pines and some other plants, in two steps: Diels-Alder reaction with maleic anhydride and reaction with p-aminophenol with a global yield of 41%. Bz22 could not be prepared by a solventless method due to the high melting point of MAI. 75 Thermal polymerization behaviour of Bz22 was influenced by the steric hindrance of the hydrogenated phenantrene ring, showing higher polymerization temperatures than conventional mono-functional benzoxazines. On the other hand, the resulting polymers exhibited outstanding thermal stability and char yield.

80 As mentioned above, DPA is the most outstanding example of synthetic partially biobased phenol exploited by benzoxazine technology. DPA is a condensation product of phenol and levulinic acid, a cheap platform chemical that can be commercially produced from cellulose-rich biomass (especially 85 from waste biomass).[47] The research interest resulted from that DPA has a structure similar to BPA, a key industrial monomer under health concerns. Our group reported the preparation of two benzoxazine monomers Bz23 (R=H and CH₃) from DPA and DPA methyl ester, respectively.[48] The thermal activated 90 polymerization of both monomers was investigated and compared to BPA-derived benzoxazine. As expected, Bz23 (R=H) could be polymerized at lower temperatures due to the presence of carboxylic acid group. Interestingly, both DPA-derived monomers afforded thermosetting polybenzoxazines 95 with higher T_g, 270 and 208ºC respectively, and higher crosslinking density compared to BPA-derived system (T_g= 172ºC). These results were attributed to the transesterification
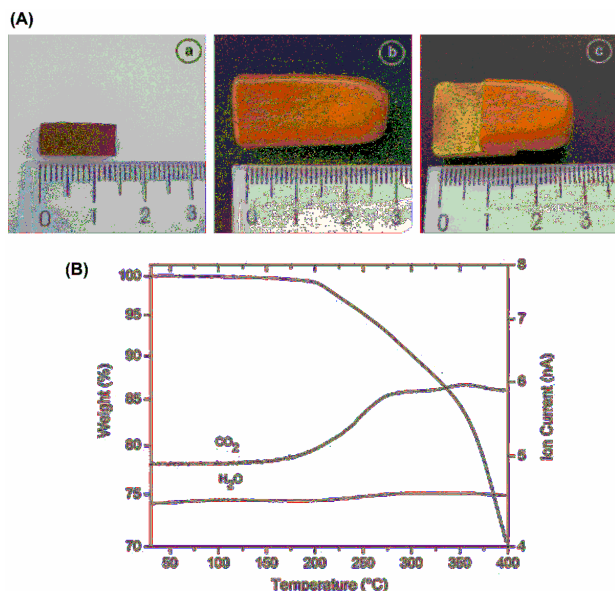
Figure 7 (A) Photographs of a) partially cured polybenoxazine Bz23 (R=H), b) polybenzoxazine foam prepared at 220ºC, and c) cross-section of this material. (B) TGA-MS analysis of foam precursor polybenoxazine Bz23 (R=H).

or esterification reactions occurred during curing process on basis to FTIR data. In addition, Bz23 (R=H) enabled the preparation of rigid foams as well as flame retardant counterparts through a self- induced foaming process.[49,50] The foaming approach described relies on the *in situ* generation of CO_2 via decarboxylation during the thermal curing. As can be seen in Figure 7, the gases evolved during the foaming process increased the volume of the original sample around 25 times under the studied conditions. At the same time, a decreasing of the material's density from 1221 ± 0.6 to 8.6 ± 0.9 kg/m^3 was measured. For the methylester derivative benzoxazine Bz23 (R=CH$_3$), fiberglass reinforced materials were obtained with flame retardancy properties. [51] Moreover, by adding neat carbon nanotubes, nanocomposite materials were prepared with low percolation threshold and improved thermal and fire properties.[52]

Concluding remarks

The growth of polybenzoxazine technology has been linked to petro-based feedstocks from birth. However, in an age of increasing oil prices, global warming, and other environmental concerns (e.g., waste), the exploration of sustainable alternative to chemicals derived from petro-based industries is the current challenge for maintaining the balance between needs of changing world while preserving the nature. Extremely versatile benzoxazine chemistry, based on phenols and amines, seems ideally suited to this quest of seeking potential molecules and subsequent conversion of naturally available materials into readily applicable polymers with desirable properties. In this line, the results presented within this contribution demonstrate that naturally occurring phenolics play and will continue to play an important route in the field of biobased polybenzoxazine research and development. However, major challenges still lie ahead. These are especially in exploring many more natural compounds and studying deeply the relationship between the structure/properties of polybenzoxazines based on them in order to identify the range of applications that can span these materials.

Gerard Lligadas was born in 1980 in Sitges (Spain) and studied chemistry at the University Rovira i Virgili (URV; Spain). In 2006, he obtained his Ph.D. under the supervision of Prof. Marina Galià and Prof. Juan C Ronda. After postdoctoral research with Prof. Virgil Percec at the University of Pennsylvania (USA) he obtained a lecturer position at URV in 2008. His research interests lie in the field of polymer design and synthesis.

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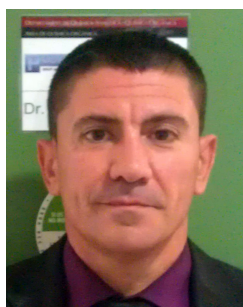
Juan C Ronda studied Chemistry at the University of Barcelona. In 1993 he obtained the PhD at the University Rovira i Virgili (URV). After two post doctoral positions (1994 and 1996) at the Case Western Reserve University in the group of Prof. Virgil Percec, he got his Habilitation at the URV. He was promoted to full professor in 2011. His current research interest focus in the synthesis of polymers starting from renewable resources using efficient synthetic methodologies.

Marina Galià received her undergraduate (BS 1987) and graduate education (PhD 1992) at the University of
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10 *and involves the synthesis of functional polymers from renewable resources.*

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20 *Professor of Organic Chemistry and in 2004 was made Distinguished Professor. She is the founding head of the Polymer Group where she initiated, built up and supervised significant research projects. Recently, her interest is in sustainable polymer chemistry: halogen-free flame retardant*
25 *thermosets, and polymers from renewable resources, using efficient synthetic procedures.*
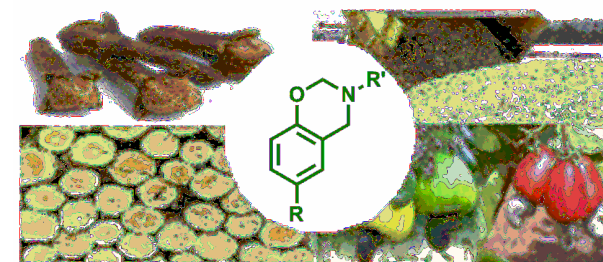
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Acknowledgements

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