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High performance bio-based benzoxazine networks from resorcinol and hydroquinone

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ABSTRACT

This work presents a scalable and solventless synthesis of two fully bio-based bis-benzoxazine resins derived from resorcinol, hydroquinone and furfurylamine. The structures of the two synthesized precursors have been studied by ^{1}H NMR and FTIR spectroscopies and SEC. The polymerization and degradation of the precursors have been investigated and monitored by DSC and TGA. The properties of the resulting polybenzoxazine networks were found to be dependent on the precursor molecular structure. In both cases, an excellent thermomechanical behavior associated with high charring ability were obtained which highlights the great potential of these fully bio-based resins as new matrices for the preparation of structural composites following a sustainable approach.

1. Introduction

Benzoxazine resins are a class of phenolic resin that benefit a growing interest in the field of thermosetting materials. The characteristic functional group of these resins consists on a heterocyclic six-membered oxazine ring fused to a benzene ring. As firstly prepared by Holly and Cope in 1944 [1] they only enter the field of thermosetting materials in the 90s with the help of Ning and Ishida who popularized their synthesis by a solventless process [2,3]. These new resins offer an excellent balance of material property, combining both the specific advantages of traditional epoxy and phenolic resins. Their henceforth well-known main features are: (i) an easy thermal curing by ring-opening polymerization without the need of hardeners or catalysts, (ii) a limited shrinkage during curing, (iii) a high glass transition temperature, (iv) a low water absorption, (v) a high charring yield, vi) a low coefficient of thermal expansion and (vii) low dielectric properties [4–7]. The combination of these interesting properties makes benzoxazines an essential resin for the preparation of high-performances materials. Nevertheless, the most relevant characteristic feature of benzoxazine probably relies on the great versatility of monomers molecular design and related chemical functionality. Indeed, as they are readily synthesized by a Mannich-like condensation of an amine, a phenol, and formaldehyde, both the diversity and large choice of possible combinations of reagents allow the preparation of a very wide range of monomers, which can be used in order to tailor or reach specific properties [8]. The number of newly synthesized monomers is thus constantly increasing; however a particular interest for both the academic and industrial researches is driven on those based on renewable or sustainable organic materials as the development of

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environmentally compatible and sustainable polymers is one of the current challenges in polymer science [9]. Some bio-based benzoxazines have been already synthesized from bio-based chemicals such as diphenolic acid [10], cardanol [11,12], furfurylamine [13–15], and more recently vanillin [16] and eugenol [17–19]. Interestingly, a short review on bio-based benzoxazine has been published very recently [20]. However, benzoxazines were in most cases only partially bio-based as the counterpart of the molecule, i.e. the amine or the phenol was still petroleum-based derivatives. To the best of our knowledge, only few groups have successfully synthesized fully bio-based benzoxazines. The renewable benzoxazine monomers reported in the literature were synthesized from the combination of furfurylamine or stearylamine with guaiacol [14,21] or furfurylamine with vanillin [22]. Such chemicals can indeed be entirely derived from bio-based feedstocks, while paraformaldehyde can be obtained from bio-methanol as mentioned by these authors. Nonetheless, these monomers consist only on monobenzoxazines and their polymerization cannot lead to a highly crosslinked network. Consequently the thermomechanical properties of these fully bio-based thermosets are almost limited by their glass transition temperature.

In order to synthesize fully bio-based benzoxazines with suitable properties for the preparation of high performance materials, two diphenolic compounds were selected and combined with furfurylamine:. resorcinol and hydroquinone, respectively benzene-1,3-diol and benzene-1,4-diol. They have been to the best of our knowledge never used for the synthesis of bisbenzoxazine resins. Kiskan and Yagci [23] used resorcinol in order to prepare a monobenzoxazine with a photopolymerizable coumarin group while Oie et al. studied the use of methylresorcinol as a crosslinker for conventional mono benzoxazine. Surprisingly, resorcinol and hydroquinone were not used as potential bio-based bisphenol, probably because they were usually known to be produced from petroleum-derived and carcinogenic benzene. However, in the 2000s alternative biosynthesis processes of these bisphenol have emerged. These interesting new approaches were studied by Frost et al. and consist on the microbial synthesis of phloroglucinol or quinic acid using glucose as raw materials, which are further catalytically converted into resorcinol or hydroquinone [24–26]. Together with catechol, these dihydroxy aromatic precursors can be thus synthesized from nontoxic plant-derived glucose following a sustainable way.

In this contribution, we report for the first time the synthesis of two novel fully bio-based bis-benzoxazine precursors using a straight and upscalable solventless method and show their potential for the preparation of high performance materials.

2. Experimental

2.1. Materials

Furfurylamine (99%), resorcinol (99%), hydroquinone (99%) and paraformaldéhyde (95%) were purchased from Aldrich and used without any further purification.

2.2. Characterizations

The ^{1}H NMR spectra were recorded with an NMR spectrometer (Bruker, 500 MHz), using deuterated dimethylsulfoxide (DMSO-d_6) as solvent and the chemical shift was calibrated by setting the chemical shift of DMSO as 2.50 ppm.

Calorimetric studies were carried out at a heating rate of 10 °C/min using a differential scanning calorimeter (DSC Q200 from TA Instruments) under nitrogen flow of 50 mL/min. An Indium standard was used for calibration.

Thermomechanical properties were investigated using a dynamic mechanical thermal analysis (DMTA) apparatus (DMA 2980 Dynamical Mechanical Analyzer from TA Instruments). Specimens ($70 \times 12 \times 3$ mm^3) were tested in a dual cantilever configuration with a dual cantilever length of 35 mm. The thermal transitions were studied in the temperature range of 25–370 °C at a heating rate of 3 °C/min and at a fixed frequency of 1 Hz. An amplitude of 18 μm was used corresponding to a strain of 0.043%. One representative sample was used for the measurements.

Thermogravimetric analysis (TGA) was used to study the anaerobic thermal degradation of the cured systems. Approximately 10 mg of the sample was submitted to a temperature ramp from 25 to 1000 °C at a heating rate of 10 °C/min under a nitrogen flow of 60 mL/min. All TGA experiments were performed by using a TGA Q50 device from TA Instruments.

Gel Permeation Chromatography (GPC) was performed in $CHCl_3$ at 35 °C using a Polymer Laboratories liquid chromatograph equipped with a PL-DG802 degasser, an isocratic HPLC pump LC 1120 with a flow rate of 1 ml/min, a differential refractive index detector ERMA 7517, and two PL gel Mixed-B 10 μm columns. PS standards were used for calibration.

Fourier transform infrared (FTIR) spectra were recorded in transmission mode using a Bruker IFS 66v/S spectrometer equipped with a vacuum apparatus. Precursors and crosslinked polymers were powdered and dispersed into a KBr matrix with a weight concentration of about 1 wt%. Spectra were recorded under vacuum from 500 to 4000 cm^{-1} with a wavenumber resolution of 4 cm^{-1}. 64 scans were collected for each sample.

2.3. Preparation and characterization of resorcinol-based benzoxazine precursor, R-Fa

This procedure stems from the ones described by Ishida et al. [3] but the addition order of reagents was changed in order to prevent the condensation reaction between bisphenols and formaldehyde and the subsequent formation of phenol–formaldehyde resin. Resorcinol 20 g ($1.798 \cdot 10^{-1}$ mol) and furfurylamine 35.3 g ($3.596 \cdot 10^{-1}$ mol) were mixed with a

mechanical agitator at 120 °C in a long 250 mL beaker until the complete dissolution of resorcinol. Paraformaldehyde, in excess of 10%, 25 g ($7.9 \cdot 10^{-1}$ mol), was then rapidly introduced under vigorous stirring in order to limit the bubbling due to the rapid decomposition of paraformaldehyde into formaldehyde. The mixture was then allowed to react for 25 min under continuous stirring. The crude reaction product was subsequently degassed for 10 min under vacuum at 140 °C on a large surface in order to remove the water formed by the condensation reaction of benzoxazine ring formation, and possible residual formaldehyde. A light yellow translucent vitrified resin, 60 g (weight yield ~95%), with a T_g at *ca.* 65 °C and an apparent polymerization enthalpy of 260 J g^{-1} was obtained. The precursor obtained from the above procedure is a mixture of R-Fa isomers **1** and **2**, namely 3,7-bis(furan-2-ylmethyl)-3,4,7,8-tetrahydro-2*H*,6*H*-[1,3]oxazino[5,6-*g*][1,3]benzoxazine and 3,9-bis(furan-2-ylmethyl)-3,4,9,10-tetrahydro-2*H*,8*H*-[1,3]oxazino[6,5-*f*][1,3]benzoxazine with also the presence of some oligomers. No further purification was carried out.

2.4. Preparation and characterization of hydroquinone-based benzoxazine precursor, H-Fa

The synthesis procedure is the same as described for the R-Fa precursor. The stoichiometric ratio for hydroquinone: CH_2O: furfurylamine was 1: 4.4: 2, while the reaction was carried out on 20 g of hydroquinone. After the degassing step, a light yellow resin was obtained and showed a beginning of crystallisation, which let expect a high degree of purity (weight yield ~95%). The H-Fa resin precursor showed a T_g at *ca.* 5 °C, a melting enthalpy of 30 J g^{-1} with a T_m^{peack} of 145 °C and an apparent polymerization enthalpy of 200 J g^{-1}. The resin is composed of a mixture of H-Fa isomers **3** and **4** with their respective IUPAC names 3,8-bis(furan-2-ylmethyl)-2,3,4,7,8,9-hexahydro[1,3]oxazino[6,5-*g*][1,3]benzoxazine and 2,9-bis(furan-2-ylmethyl)-1,2,3,8,9,10-hexahydro[1,3]oxazino[5,6-*f*][1,3]benzoxazine. No further purification was carried out.

2.5. Curing of R-Fa and H-Fa resins

All the precursors were introduced in a stainless steel mold, molten, further degassed in a vacuum oven at 140 °C during 10 min, and then step cured in an air-circulating oven according to the following cycle: 1 h at 140 °C, 2 h at 180 °C, 2 h at 200 °C, 1 h at 220 and 30 min at 230 °C. Thereafter, samples of $80 \times 12 \times 3$ mm^3 were allowed to slowly cool down to room temperature before their unmolding.

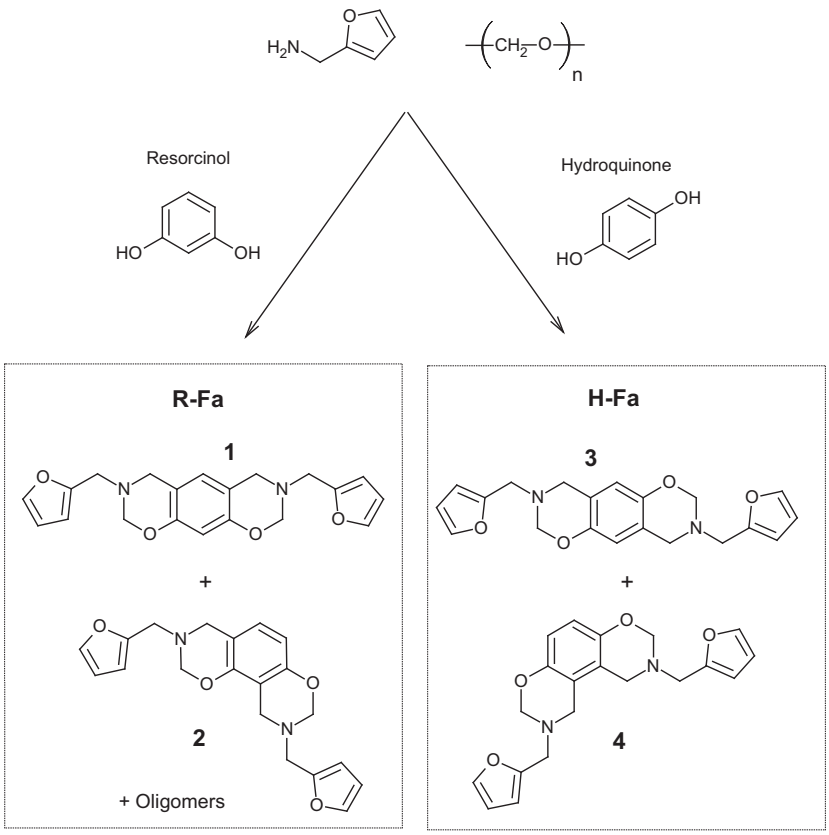
3. Results and discussion

3.1. Synthesis and characterization of crude precursors

R-FA and H-Fa resin precursors were successfully prepared by a solventless synthesis from furfurylamine and either resorcinol or hydroquinone, with a straight and scalable procedure according to the reactions depicted in Scheme 1.

The structure of the new benzoxazine H-Fa was investigated by ^{1}H NMR as shown in Fig. 1. The attribution of resonance signals was based on the analysis of ^{1}H NMR spectra of reagents and on the previous study of furfurylamine-based benzoxazines [14]. The peaks around 3.8 ppm and 4.7 ppm may be attributed to the Ph—CH_2—N and O—CH_2—N of oxazine ring respectively and thus verify the formation of benzoxazine. Additional peaks labelled *a*, *b*, *c* and *d*, with resonances at 7.06, 6.42, 6.34 and 3.68 ppm attest for the formation of the desired benzoxazine structure containing the furan moiety. Comparison of the overall integral values of aromatic protons and methylene units shows firstly that benzoxazine rings are not opened and secondly that the furan ring has not reacted during the synthesis. An additional information supporting the absence of polymerized structure is provided by the absence of resonance signal that could be assigned to Mannich-type linkage in the methylene proton area [27]. Thus the synthesis procedure is clearly robust enough to produce H-Fa without leading to oligomerization of the reactive resin. Negligible amount of residual furfurylamine can be detected by the very limited intensity resonance peaks showing up at 3.61, 6.18, 6.37 and 7.57 ppm. Another interesting observation is provided by the splitting of peaks *e*, *f*, and *g* that gives rise to the emergence of peaks *e*′, *f*′ and *g*′ respectively. This splitting is due to the formation of the two isomeric species **3** and **4** as depicted in Scheme 1. A rough comparison of integrals demonstrates a prevalence of the isomeric form **4** (70%) on the isomer **3** (30%). Resonance signal assignments were achieved with the help of ^{1}H NMR simulation. The reasons of the predominance of species **4** are not clearly evidenced yet, but Fields et al. have also reported a predominance of a type **4** isomer for hydroquinone-based benzoxazines even though the formation of this type of isomer is not favoured by steric hindrance [28]. Several factors, such as the type of amine or the synthesis conditions could affect the ratio of the two isomers and the proportion could be even reversed as interestingly highlighted by these authors.

Concerning the R-Fa precursor, as can be observed on the ^{1}H NMR spectrum depicted in Fig. 2, the monomer structure is not as well defined as the H-Fa one. Indeed, the resonance peaks are broadened and overlapped and do not allow a clear distinction of isomeric species. Nevertheless, both the characteristic peaks of the furan moiety *a*, *b*, *c* and *d*, and the benzoxazine ring *e* and *f* attest for the formation of the desired precursors. The broadening of each peak highlights some partial oligomerization of the monomers. This simultaneous partial polymerization is also evidenced by the emergence of phenolic hydroxyl protons as shown by the broad resonance peak *j* with a chemical shift at about 10.8 ppm. The number of opened benzoxazine rings cannot be accurately determined as the overall methylene proton resonance peaks are overlapped with the peak of water at 3.3 ppm. The crude R-Fa precursor is then constituted of a mixture of the monomers and some related oligomers.



Scheme 1. One pot synthesis of R-Fa and H-Fa precursors.

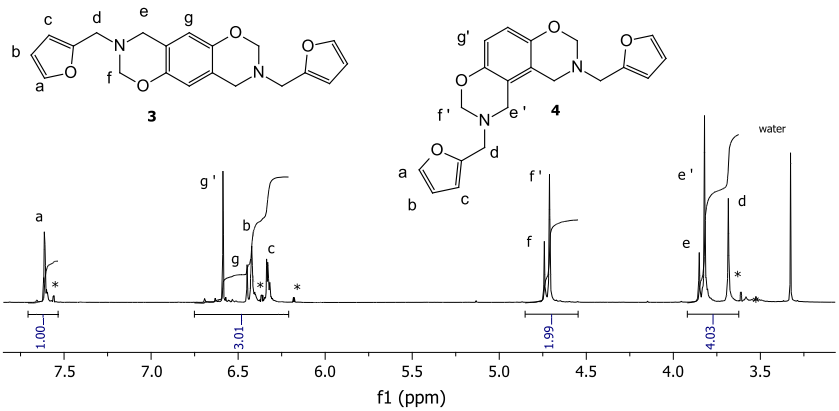


Fig. 1. ^{1}H NMR spectrum of H-Fa precursor obtained after the degassing step. DMSO-d_6. 500 MHz, 25 °C. Residual furfurylamine characteristic peaks labelled ∗.

Due to the lower resolution of its NMR spectrum, the study of the composition of the R-Fa precursor was further completed by size exclusion chromatography analysis (SEC). As can be seen on Fig. 3, while the H-Fa resin is mainly composed of monomers with a single elution peak around 18.2 min, the chromatogram of the R-Fa precursor displays, in addition to the monomer elution peak (18.2 min), a broad shoulder at shorter retention time, which clearly indicates the presence of oligomers and higher molecular weight species. A rough deconvolution of this signal into two populations lets expect a proportion of oligomers of about 40%. Therefore, in the same synthesis conditions the side opening reaction of benzoxazine ring of the R-Fa resin partly occurs, traducing a higher reactivity due to the *meta* substituted bisphenol instead of the *para* one. Properties and reactivity of both precursors were then characterized by DSC and TGA.

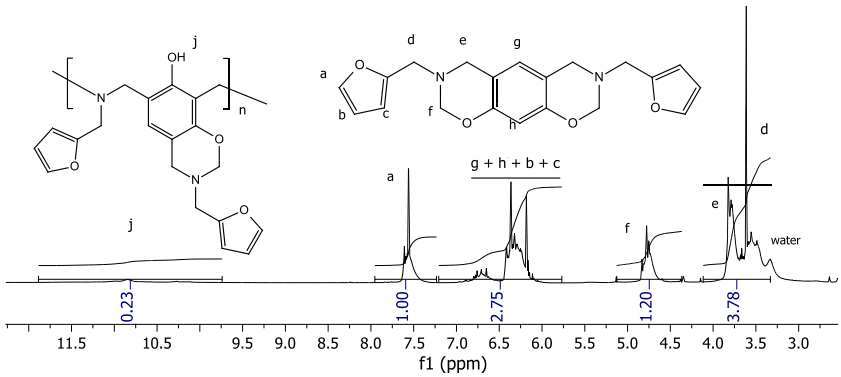


Fig. 2. ^{1}H NMR spectrum R-Fa precursor obtained after the degassing step. DMSO-d_6, 500 MHz, 25 °C.

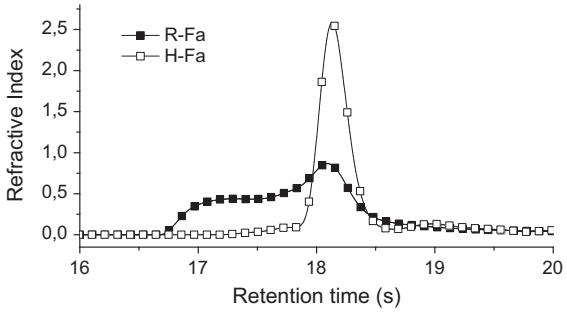


Fig. 3. SEC chromatograms of R-Fa and H-Fa precursors. $CHCl_3$.

DSC thermograms shown in Fig. 4 indicate a T_g at *ca.* 5 °C and 65 °C for H-Fa and R-Fa precursors, respectively. This difference of 60 °C is due to the oligomerization of the R-Fa resin. An evidence of the purity of the H-Fa resin is given by its aptitude to crystallize as demonstrated by the small endothermic peak of nearly 30 J/g located around 140 °C. When comparing the two exothermic peaks associated to the crosslinking reaction, differences are observed. The first one lies in the variation of the beginning of the exotherm, which occurs at a lower temperature in the case of R-Fa; i.e., 200 °C instead of 225 °C for the H-Fa. Likely such an observation is partly due to the catalytic effect of phenols present in oligomers, which are formed by the ring opening (Fig. 2). This catalytic effect is well known in case of benzoxazine reactions [29,30].

In addition, the enthalpy value of the polymerization reaction is higher in the case of R-Fa with a ΔH of 250 J g^{-1}, which corresponds to 44.3 kJ per mole of benzoxazine ring. This value diverges from the one usually accepted for benzoxazine, i.e., 73 kJ per mole of benzoxazine ring as recorded early by Ishida et al. on the bisphenol-A based benzoxazine [29]. However, as the R-Fa precursor is composed of nearly 40% of oligomers, this value appears to be in good accordance with the results obtained by SEC as it represents a percentage of unopened benzoxazine cycles of 60%. In addition, it can be mentioned that

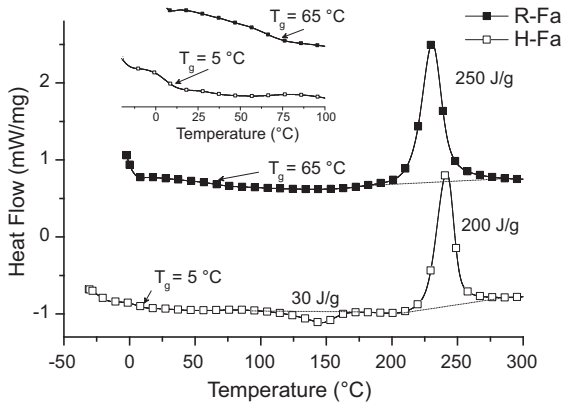


Fig. 4. DSC thermograms of R-Fa and H-Fa precursors. Inset: zoom on the precursors glass transition temperatures.

the furan moiety can participate into the polymerization mechanism as reported by Endo and his coworkers [14,21]. The different reaction mechanisms appear then to be combined in one single enthalpic exotherm. Concerning the H-Fa resin, the enthalpic crosslinking exotherm is observed at a lower temperature by about 20% and the exothermic peak is overlapped with a partial degradation of the monomer, known to occur in the same temperature range. These degradations are shown in the TGA profiles depicted in Fig. 5.

Such a monomer degradation process is scarcely reported in the literature. Nevertheless, the thermal degradation of bisphenol-A based benzoxazine has been recently studied and correlated with the evolution of a zwiterionic intermediate. An equilibrium between two species is established during the polymerization, the first species favors the polymerization while the second one leads to the dissociation of the amino moiety and the subsequent release of a volatile imine [31–34]. In the case of H-Fa, the phenomenon is exacerbated with a weight loss of 31% instead of the 7% recorded for the R-Fa upon the polymerization temperature range and under nitrogen flux. Nevertheless, it is worth noting that the weight loss recorded by TGA has not a dramatic effect on the resin curing since the resin is cured in bulk. Indeed, in bulk, the observed weight losses become negligible and do not lead to the formation of uncontrollable defects.

The structural changes of the resin that occur during the curing were monitored by FTIR. The spectra of the studied systems before and after curing are presented in Fig. 6. Assignments of absorbance peaks are quite delicate as they easily overlap and as the spectral resolution is severely affected by the crosslinking of the resin. The main absorbance peaks were identified with the help of literature [13,14,35–38].

The benzoxazine rings were observed for both R-Fa and H-Fa precursors with the characteristic absorptions at 1230 cm^{-1} (asymmetric stretching of C—O—C), 1085 cm^{-1} (asymmetric stretching of C—N—C), and 1345 cm^{-1} (CH_2 wagging into the closed benzoxazine ring). The absorption band at 1450–1500 cm^1 was assignable to the tetrasubstituted benzene groups in benzoxazine molecules. The absorption bands located at 1116 and 930 cm^{-1} are due to the C—H in plane bonding vibration (mod 18b) and C—H out of plane deformation (mod 10a), respectively [35]. The furan groups in both compounds were observed with the absorption peaks at 1506 and 980 cm^{-1}, this last one did not suffer too much overlapping from other resonance peaks [13,14]. By the way, as can be seen in Fig. 6, the spectrum of R-Fa precursor is less detailed than the one of H-Fa. Peaks are broader and a new absorption band at 1618 cm^{-1} appears, which may be attributed to aromatic C=C stretching vibrations of benzene ring with a higher degree of substitution and intermolecular hydrogen bonding [39,40]. Moreover, the furan characteristic absorption peaks present a lower intensity in the case of R-Fa precursors. These results tend to show the beginning of the polymerization of the R-Fa resin, with a partial implication of the furan group in good agreement with ^1H NMR and SEC results.

After the curing step, the absorption bands at 930 and 1345 cm^{-1} disappeared confirming the ring-opening reaction of benzoxazine and the formation of Mannich-type bridge structures with the simultaneous disappearance of the peak at 1116 cm^{-1} corresponding to C—H bond attached to the aromatic structure. The absorption band located around 1618 cm^{-1} has severely increased and the bands around 1500 cm^{-1}, characteristic of the substituted benzene ring, have shifted to lower wavenumbers witnessing a variation of the degree of substitution of the benzene ring. The presence of the large absorption band at 3000–3500 cm^{-1} is also an additional evidence of the benzoxazine polymerization as it produces phenol entities. In addition, the decrease of the peak intensity of the furan group at 980 cm^{-1} finally confirms its involvement into the crosslinking reaction as proposed by Wang et al. [21] for a benzoxazine containing a furan moiety as illustrated by the Scheme 2.

3.2. Properties of the bio-based cured benzoxazines

Crosslinked polybenzoxazine networks were prepared by curing R-Fa and H-Fa precursors according to the conditions described in the Experimental Section and led to samples of dark-brown color. The determination of the glass transition temperature (T_g) was not possible using conventional DSC measurements as no significant calorimetric capacity variation

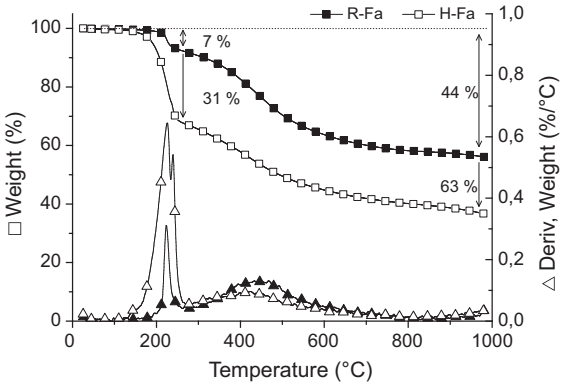


Fig. 5. TGA profiles of R-Fa and H-Fa precursors under nitrogen.

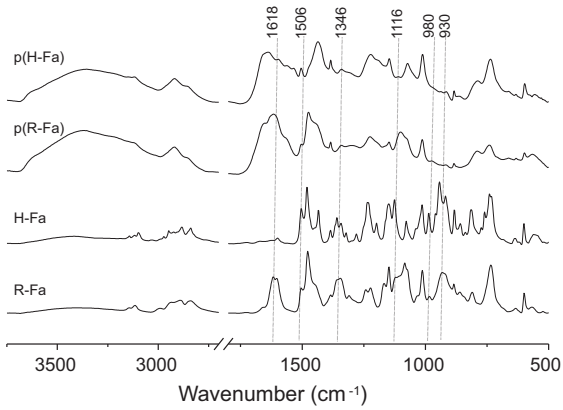
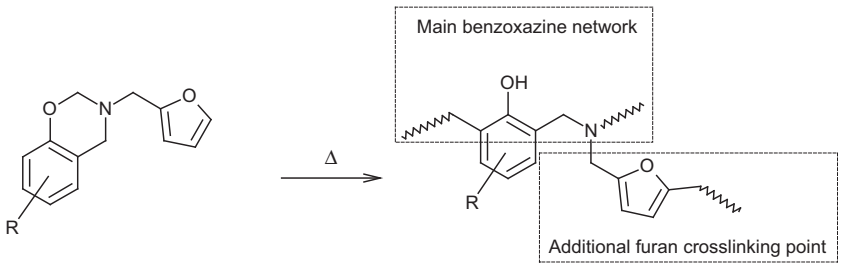


Fig. 6. FTIR spectra of R-Fa and H-Fa precursors and their respective crosslinked polymers p(R-Fa) and p(H-Fa).

was observable for the cured samples. The mechanical transition temperature T_α associated to the T_g was thus evaluated using thermomechanical analysis. As can be seen on Fig. 7, both thermosets have an excellent thermomechanical behavior with T_α higher than 250 °C. The thermomechanical stability is set up to 230 °C for the p(H-Fa) and up to 270 °C for the p(R-Fa) as the storage modulus G′ is maintained in the glassy state until these temperatures before its drop associated to the T_g. The maximum of tan δ peak is recorded around 280 °C in case of p(H-Fa) while it is observed as *ca.* 300 °C for the p(R-Fa). In this last case the T_α is so high that it is superimposed with the beginning of the thermal degradation (see Fig 8). The storage modulus in the glassy state is comparable for the two crosslinked polymers with a value of about 3.7 GPa at 25 °C but its gradual decrease with temperature is more pronounced in case of p(H-Fa). Moreover, the transition area between the glassy and rubbery state appears to be larger for the p(H-Fa) providing evidence for a more heterogeneous network with different relaxation times [41]. Based on the rubbery elasticity theory [42], the difference of the storage modulus values measured in the rubbery state, *i.e.*, above the glass transition, shows a higher crosslinking density in case of p(R-Fa). Thus it seems that the monomeric structure of the R-Fa resin based on the *meta*-benzene diol allows for the formation of a denser network although both precursors present the same chemical composition and were cured within identical conditions. We are actually working on this aspect in order to elucidate the reasons of the observed differences. Nevertheless, the thermomechanical properties of these two new fully bio-based polymer networks allow them from being considered as high performance matrices with intrinsic thermomechanical stability higher than the values reported for the traditional bisphenol-A based benzoxazine (T_g at *ca.* 160 °C) [43] and far higher the ones of fully bio-based benzoxazines prepared with guaiacol and furfurylamine (T_g at *ca.* 150 °C) [14,21]. Sini et al. [22] synthesized also a fully bio-based benzoxazine prepared with vanillin and furfurylamine. They proposed a T_g of 270 °C for the cured resin but no DSC nor DMA graphs were provided. Additionally, the vanillin based monomer suffered a severe degradation upon the curing temperature range with a weight loss of nearly 20% at 250 °C due to the release of CO_2. As a result, this type of resin will form a material exhibiting dramatic porosity when cured in bulk [22,44].

Interestingly, the thermal stability of the polybenzoxazines was investigated by thermogravimetric analysis under anaerobic conditions. As shown on Fig. 8, both TGA thermograms are very similar with high charring ability. Indeed, at 1000 °C, the char content of the two materials is as high as 60 wt% making them particularly attractive for the preparation of ablative composite materials [45]. This high charring ability is due to the intrinsic phenolic structure of the crosslinked polybenzoxazine with high degree of aromaticity and could be also enhanced by the reactivity of the furan moiety, which promotes additional extent of crosslinking [8,14]. Indeed, the extra crosslinking reaction provided by the furan moiety may suppress segmental decomposition into gaseous fragments as the thermal decomposition of polybenzoxazine is usually known to begin with the cleavage of the amino part [34].



Scheme 2. Illustration of the possible additional crosslink provided by the furan group in accordance with Wang et al. [21].

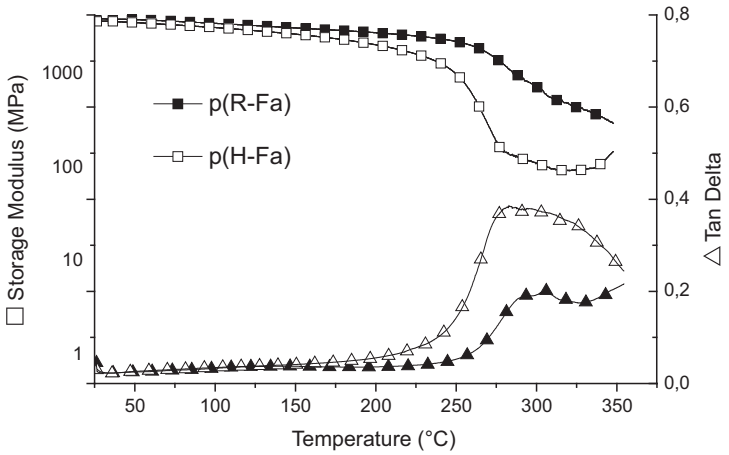


Fig. 7. Evolution of the thermomechanical behavior of p(R-Fa) (closed symbols) and p(H-Fa) (open symbols). Frequency: 1 Hz, Temp ramp rate: 3 °C min^{-1}.

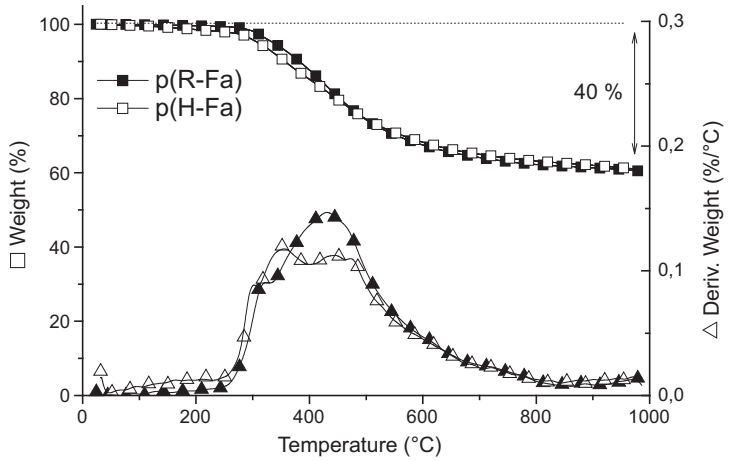


Fig. 8. TGA profiles of p(R-Fa) and p(H-Fa) obtained under nitrogen at 10 °C min^{-1}.

By a more accurate characterization of the TGA profiles, some differences between the two resins may be detected. The degradation of the p(H-Fa) seems to start at a lower temperature with a temperature at a weight loss of 5% $T_{d5\%}$ of 310 °C instead of the 335 °C recorded for the p(R-Fa) with a main degradation occurring at 355 °C for the p(H-Fa) instead of 430 °C for the p(R-Fa). These differences are quite consistent with the lower degree of crosslinking produced by the hydroquinone-based benzoxazine as evidenced by the aforementioned DMA measurements. Despites these modest differences, both resins present excellent thermal stability, and their high charring lets expect improved fire properties with intrinsic values of limiting oxygen index higher than 40% according to the well-known Van Krevelen and Hofwitzer method [46].

4. Conclusion

Two fully bio-based bis-benzoxazines have been synthesized by a solventless and scalable method without the need of additional purification. The synthesis of hydroquinone-based benzoxazine leads to a mixture of isomers with a high degree of purity while the resorcinol based precursors contain some oligomers due to a higher reactivity of the reagents. Both precursors allow for the formation of highly crosslinked network with an active participation of the furan group into the polymerization. The two cured thermoset systems exhibit excellent thermomechanical properties with glass transition temperatures higher than 280 °C and present remarkable inherent charring ability upon pyrolysis. Better properties were observed for the resorcinol-based benzoxazine, which were correlated to a higher crosslinking density of the resulting network. The possibility to prepare high performance thermoset materials by using only renewable resources in an easy synthesis procedure has been demonstrated. The combination of excellent thermomechanical and thermal properties with the bio-based connotation makes these resins promising candidates for the preparation of the next generation thermosetting materials especially in the framework of the increasingly demand from industries, which look forward to subscribing to sustainable approaches without sacrifying the material properties [47,48].

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