

Phloretic acid-based multi-benzoxazine monomers: tetramethyl guanidine-assisted synthesis and thermal crosslinking

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ABSTRACT

An efficient strategy to synthesize biobased multi-functional benzoxazine compounds was developed using the 1,1,3,3-tetramethyl guanidine (TMG)-triggered esterification reaction of carboxylic acids with organic halides as a key synthetic step. The biobased phloretic acid was combined with either aniline or furfurylamine to prepare the corresponding carboxylic acid-functional monobenzoxazine monomers. Next, the use of TMG enabled the esterification of these compounds with di-, tri- and tetra-functional benzyl bromide compounds at room temperature to afford a series of multi-benzoxazine monomers tethered to an aromatic core. The effect of monomers functionality on the curing process was analyzed, indicating that the reactivity in the thermally induced ring-opening increases with the number of furan and oxazine rings in the monomers. The resulting thermosets revealed good correlation between the number of oxazine rings in the structure of the monomer and the properties of the crosslinked materials. Regarding the furfurylamine-based polybenzoxazines, they showed improved thermal behavior compared to the aniline-based resin, due to the role of furan rings. All materials showed high T_g s, good thermal stability, and flame retardancy properties.

Keywords: polybenzoxazines, renewable resources, phloretic acid, triggered esterification

1. INTRODUCTION

Benzoxazines are a novel class of chemical structures that allow the generation of high-performance thermosetting phenolic polymers. These monomers exhibit six-membered oxazine rings in their chemical structures. Among the possible isomers, 1,3-benzoxazines are of interest in the field of polymers due to its thermally-induced ring opening polymerization. Usually, 1,3-benzoxazine monomers are synthesized by a Mannich-type condensation reaction between formaldehyde, phenolic compounds and primary amines in a molar ratio of 2:1:1, respectively [1]. One of the most interesting characteristic of the benzoxazine chemistry is that it offers high molecular design flexibility, allowing them possible to form materials with targeted properties [1,2]. In addition, their crosslinked materials, i.e. polybenzoxazines, exhibit outstanding characteristics such as low flammability, good chemical and thermal resistance, excellent dimensional stability, among others [3].

Due to the environmental and sustainable economic concerns, in the last decades both academic and industrial sectors have engaged in exploring the design of biobased polybenzoxazines, since trials on developing other biobased polymers succeeded and are already available in market [4]. Until now, most efforts focused on deriving phenols from renewable biomass, i.e. arbutin, coumarin, lignin derivatives, eugenol, among others[5–16], as well as biobased amines such as furfurylamine and amino acid into mono- and bis-oxazine precursors[17–19]. However, the limitation of having natural biobased multi-phenols and/or multi-amines has restricted the development of benzoxazine monomers with oxazine ring functionality greater than two, and only few monomers were developed[8,20,21].

Phloretic acid, a carboxylic acid-containing phenolic compound which can be extracted either by enzymatic or chemical treatment of phloretin or by hydrogenation of *p*-coumaric acid from lignin [22], has already been demonstrated to be a promising biobased building block to prepare advanced polybenzoxazine precursors. Comí *et al.* prepared monofunctional benzoxazines by reaction between phloretic acid and aniline [23]. The resulting materials exhibited excellent thermal properties. Subsequently, Kirubakaran *et al.* synthesized a furfurylamine-phloretic acid-based benzoxazine with low polymerization temperature [24], obtaining materials with good thermal properties. More recently, Trejo-Machin *et al.* also exploited the difunctional nature of phloretic acid to synthesize highly processable

difunctional benzoxazine monomers via enzymatic esterification of polyethyleneglycols. The resulting benzoxazine precursors, especially when prepared using furfurylamine as amine component, resulted in highly competitive thermosets [25]. In this line, we envisaged that the 1,1,3,3-tetramethyl guanidine (TMG)-assisted nucleophilic substitution reaction between carboxylic acids and activated alkyl halides would be an efficient tool to prepare innovative multifunctional benzoxazine scaffolds based on phloretic acid. As guanidine groups are highly basic ($pK_a = 12.3$), these have found many applications in the preparation of nonviral polymeric vectors and as a catalyst in organic synthesis [26–29]. In this context, TMG has demonstrated to trigger the esterification reaction of carboxylic acids with alkyl halides under mild conditions, i.e. room temperature [32–35]. This efficient reaction has recently been exploited in rapid and high-yielding monomer and polymer synthesis routes based on sustainable renewable resources [30–32]. Herein, we envisaged that could also be used to deliver multifunctional, i.e. di-, tri- and tetra-polybenzoxazine precursors based on phloretic acid. Hence, studies of tetramethyl guanidine-assisted phloretic acid-based multi-benzoxazines synthesis and thermal crosslinking are presented on the following paragraphs. The relationship between the oxazine functionality degree and thermal, mechanical, and flame retardant properties of the resulting thermosetting polymers is also investigated.

2. EXPERIMENTAL SECTION

2.1. Materials

3-(4-hydroxyphenyl)propionic acid (phloretic acid, Ph), 1,1,3,3-tetramethyl guanidine (TMG), 1,3,5-tris(bromomethyl)benzene (Bn3Br), α,α' -dibromo-p-xylene (Bn2Br), 1,2,4,5-tetrakis(bromomethyl)benzene (Bn4Br), furfurylamine, aniline, paraformaldehyde and 2-methyltetrahydrofuran (MeTHF) were purchased from Merck. 1,4-dioxane was provided from Cicarelli. All solvents were purified by standard procedures.

2.2. Synthesis of Benzoxazine Templates

2.2.1. 3-(3-Phenyl-3,4-dihydro-2H-1,3-benzoxazin-6-yl)propanoic acid (PhA-Bz)

The synthesis of monofunctional benzoxazine templates based on phloretic acid (Ph) was carried out adapting a previously reported two-stage procedure [23]. First, 1,3,5-

triphenylhexahydro-1,3,5-triazine was synthesized as follows: aniline (93.13 g, 1 mol) and paraformaldehyde (30.00 g, 1 mol) were added to a 250 mL two-necked round bottom flask equipped with a teflon coated stirring bar and a condenser. Toluene (75 mL) was then added to the reaction flask and the reaction mixture gradually heated up to 100 °C under continuous agitation for two hours. The resulting precipitated product was filtered and washed with small amounts of cold methanol obtaining a fine white powder, which was dried at 60 °C under vacuum.

For the synthesis of the PhA-Bz template (Scheme 1a), 1,3,5-triphenylhexahydro-1,3,5-triazine (0.74 g, 8 mmol), paraformaldehyde (0.078 g, 2.6 mmol), phloretic acid (0.43 g, 2.6 mmol) and 250 mL of 2-methyltetrahydrofuran (MeTHF) were placed into a 500 mL two-necked round bottom flask equipped with a condenser and a Teflon-coated stirring bar. The reaction mixture was gradually heated at 75 °C during 16 h. The resulting product was filtered, concentrated and purified by recrystallization twice with diethyl ether, obtaining a yellow fine powder with 95% yield.

¹H-NMR (CDCl₃, tetramethylsilane (TMS), δ ppm): 2.62 (2H, t, CH₂-Ar), 2.85 (2H, t, CH₂-COO), 4.60 (2H, s, Ar-CH₂-N), 5.33 (2H, s, O-CH₂-N), 7.28–6.73 (8H, ArH).

¹³C-NMR (CDCl₃, δ ppm): 29.8 (CH₂-Ar), 35.8 (CH₂-CO), 50.4 (Ar-CH₂-N), 79.4 (O-CH₂-N), 117.0 (Ar), 118.3 (Ar), 120.8 (Ar), 121.5 (Ar), 126.4 (Ar), 127.7 (Ar), 129.3 (Ar), 132.5 (Ar), 148.4 (Ar), 152.8 (Ar), 178.0 (C=O).

2.2.2. 3-furfuryl-3-(3-phenyl-3,4-dihydro-2H-1, 3-benzoxazine-6-yl) propanoic acid (PhF-Bz)

PhF-Bz was synthesized following previously reported procedures [24], and the general synthesis route is depicted in Scheme 1b. Furfurylamine (0.24 g, 2.5 mmol), paraformaldehyde (0.15 g, 5 mmol), phloretic acid (0.41 g, 2.5 mmol) and 50 mL of 1,4-dioxane were placed into a 100 mL two-necked round bottom flask equipped with a condenser and a Teflon-coated stirring bar. The reaction mixture was stirred and heated at 100 °C for 16 h. The resultant product was purified by recrystallization twice using diethyl ether as solvent, then dried under vacuum to obtain white solid with a 85% yield.

^1H -NMR (CDCl_3 , tetramethylsilane (TMS), δ ppm): 2.7 (2H, t, $\text{CH}_2\text{-COOH}$), 2.9 (2H, t, $\text{CH}_2\text{-CH}_2$), 3.9 (2H, s, $\text{N-CH}_2\text{-Ar}$), 4.1 (2H, s, $\text{CH}_2\text{-N}$), 4.9 (2H, s, $\text{O-CH}_2\text{-N}$), 6.3–7.5 (6H, ArH).

^{13}C -NMR (CDCl_3 , δ ppm): 30.4 ($\text{CH}_2\text{-Ar}$), 34.8 ($\text{CH}_2\text{-CO}$), 53.0 ($\text{N-CH}_2\text{-furan}$), 56.4 ($\text{Ar-CH}_2\text{-N}$), 80.4 ($\text{O-CH}_2\text{-N}$), 110.4 (aromatic furan), 110.6 (aromatic furan), 121.0 (Ar), 128.3 (Ar), 130.8 (Ar), 131.5 (Ar), 142.2 (aromatic furan), 147.7 (aromatic furan), 155.5 (Ar), 174.4 (C=O).

2.3. Synthesis of multi-oxazine benzoxazines

PhA-Bz or PhF-Bz benzoxazine precursor (1mmol) and TMG reagent (1mmol) dissolved in Me-THF or dioxane (2.5 ml) were added in a round bottom flask provided with a magnetic Teflon-coated stirring bar. After 2 min, Bn2Br, Bn3Br or Bn4Br based reagent (1:1 Br : benzoxazine salt molar ratio) dissolved in 2.5 mL of the corresponding solvent was added dropwise into reaction medium. The reaction was carried out at room temperature (25 °C), during 4 h. The resultant reaction mixture was dissolved in ethyl acetate, washed once with NaOH solution (5% w/w) and twice with distilled water. Finally, the corresponding multifunctional benzoxazine was obtained after drying the organic phase with anhydrous MgSO_4 and evaporating the solvent under vacuum.

The chemical structure of each product was verified using Infrared spectroscopy (FTIR), and Nuclear Magnetic Resonance of Proton and Carbon (^1H - and ^{13}C -NMR).

1,4-phenylenebis(methylene)bis(3-(3-phenyl-3,4-dihydro-2H-benzo[e][1,3]oxazin-6-yl)propanoate) (PhA-2Bz)

Yield: 96%; FTIR (cm^{-1}): 1750 (C=O , symmetric stretching (ν_s)), 1510 $\nu(\text{C=C}_{\text{Ar}}$, ν_s), 1305 (wagging of CH_2 , oxazine), 1228 (C-O-C , ν_{as} , oxazine ring), 1150 (C-N-C , ν_{as} , oxazine ring) and 930 ($\text{N-CH}_2\text{-O}$, out-of-plane deformation oxazine attached to aromatic ring).

^1H -NMR (CDCl_3 , tetramethylsilane (TMS), δ ppm): 2.62 (4H, t, $\text{CH}_2\text{-CH}_2\text{-C=O}$), 2.85 (4H, t, $\text{Ar-CH}_2\text{-CH}_2$), 4.56 (4H, s, $\text{N-CH}_2\text{-Ar}$), 5.08 (4H, s, $\text{O-CH}_2\text{-Ar}$), 5.32 (4H, s, $\text{N-CH}_2\text{-O}$), 6.69-7.30 (20H, m, Ar-H).

^{13}C -NMR (CDCl_3 , δ ppm): 30.5 ($\text{CH}_2\text{-Ar}$), 34.2 ($\text{CH}_2\text{-CO}$), 59.4 ($\text{Ar-CH}_2\text{-N}$), 66.2 ($\text{Ar-CH}_2\text{-O}$), 92.5 ($\text{O-CH}_2\text{-N}$), 111.5 (Ar), 114.3 (Ar), 120.4 (Ar), 121.8 (Ar), 127.3 (Ar), 128.1 (Ar), 129.5 (Ar), 131.4 (Ar), 140.4 (Ar), 149.8 (Ar), 154.5 (Ar), 173.1 (C=O).

1,4-Phenylenebis(methylene)bis(3-(3-(furan-2-ylmethyl)-3,4-dihydro-2H-benzo[e][1,3]oxazin-6-yl)propanoate) (PhF-2Bz)

Yield: 94%, FTIR (cm^{-1}): 1750 (C=O , ν_s); 1617 (C-O , ν_s , furan ring); 1510 (C=C_{Ar} , ν_s , oxazine ring); 1440 (C-H , ν_s , furan ring); 1228 (C-O-C , ν_{as} , oxazine ring); 1150 (C-N-C , ν_{as} , oxazine ring); 1010 (C-O , ν_s , furan ring, furan ring); 930 ($\text{N-CH}_2\text{-O}$, out-of-plane bending of oxazine attached to aromatic ring); and 763 (C-H , out-of-plane wagging, furan ring).

^1H -NMR (CDCl_3 , tetramethylsilane (TMS), δ ppm): 2.60 (4H, t, $\text{CH}_2\text{-CH}_2\text{-C=O}$), 2.83 (4H, t, $\text{Ar-CH}_2\text{-CH}_2$), 3.87 (4H, s, $\text{N-CH}_2\text{-furan}$), 3.93 (4H, s, $\text{Ar-CH}_2\text{-N}$), 4.82 (4H, s, $\text{N-CH}_2\text{-O}$), 5.06 (4H, s, $\text{O-CH}_2\text{-Ar}$), 6.19 (2H, d, CH-CH-C), 6.30 (2H, m, CH-CH-CH), 6.67-7.22 (10H, m, Ar-H), 7.37 (2H, m, O-CH-CH).

^{13}C -NMR (CDCl_3 , δ ppm): 30.2 ($\text{CH}_2\text{-Ar}$), 36.1 ($\text{CH}_2\text{-CO}$), 48.2 ($\text{furan-CH}_2\text{-N}$), 49.5 ($\text{Ar-CH}_2\text{-N}$), 65.8 ($\text{Ar-CH}_2\text{-O}$), 81.7 ($\text{O-CH}_2\text{-N}$), 108.9 (aromatic furan), 110.2 (Ar), 116.5 (Ar), 119.5 (Ar), 127.3 (Ar), 127.7 (Ar), 128.3 (Ar), 132.6 ppm (Ar), 136.0 ppm (Ar), 142.6 (aromatic furan), 151.6 (aromatic furan), 152.4 (Ar), 172.7 ppm (C=O).

Benzene-1,3,5-triyltris(methylene)tris(3-(3-(furan-2-ylmethyl)-3,4-dihydro-2H-benzo[e][1,3]oxazin-6-yl)propanoate) (PhF-3Bz)

Yield: 92%, FTIR (cm^{-1}): 1750 (C=O , ν_s); 1617 (C-O , ν_s , furan ring); 1510 (C=C_{Ar} , ν_s , oxazine ring); 1440 (C-H , ν_s , furan ring); 1228 (C-O-C , ν_{as} , oxazine ring); 1150 (C-N-C , ν_{as} , oxazine ring); 1010 (C-O , ν_s , furan ring, furan ring); 930 ($\text{N-CH}_2\text{-O}$, out-of-plane bending of oxazine attached to aromatic ring); and 763 (C-H , out-of-plane wagging, furan ring).

^1H -NMR (CDCl_3 , tetramethylsilane (TMS), δ ppm): 2.64 (4H, t, $\text{CH}_2\text{-CH}_2\text{-C=O}$), 2.86 (4H, t, $\text{Ar-CH}_2\text{-CH}_2$), 3.89 (4H, s, $\text{N-CH}_2\text{-furan}$), 3.95 (4H, s, $\text{Ar-CH}_2\text{-N}$), 4.84 (4H, s, $\text{N-CH}_2\text{-O}$),

5.10 (4H, s, O-CH₂-Ar), 6.23 (2H, d, CH-CH-C), 6.32 (2H, m, CH-CH-CH), 6.70-7.24 (10H, m, Ar-H), 7.40 (2H, m, O-CH-CH).

¹³C-NMR (CDCl₃, δ ppm): 30.2 (CH₂-Ar), 36.0 (CH₂-CO), 48.2 (furan-CH₂-N), 49.5 (Ar-CH₂-N), 65.7 (Ar-CH₂-O), 81.7 (O-CH₂-N), 108.9 (aromatic furan), 110.2 (Ar), 116.5 (Ar), 119.5 (Ar), 127.3 (Ar), 127.6 (Ar), 128.3 (Ar), 132.6 ppm (Ar), 136.8 ppm (Ar), 142.6 (aromatic furan), 151.5 (aromatic furan), 152.3 (Ar), 172.6 ppm (C=O).

Benzene-1,2,4,5-tetra-yltetrakis(methylene)tetrakis(3-(3-(furan-2-ylmethyl)-3,4-dihydro-2H-benzo[e][1,3]oxazin-6-yl)propanoate) (PhF-4Bz)

Yield: 93%, FTIR (cm⁻¹): 1750 (C=O, v_s); 1617 (C-O, v_s, furan ring); 1510 (C=C_{Ar}, v_s, oxazine ring); 1440 (C-H, v_s, furan ring); 1228 (C-O-C, v_{as}, oxazine ring); 1150 (C-N-C, v_{as}, oxazine ring); 1010 (C-O, v_s, furan ring, furan ring); 930 (N-CH₂-O, out-of-plane bending of oxazine attached to aromatic ring); and 763 (C-H, out-of-plane wagging, furan ring).

¹H-NMR (CDCl₃, tetramethylsilane (TMS), δ ppm): 2.53 (4H, t, CH₂-CH₂-C=O), 2.91 (4H, t, Ar-CH₂-CH₂), 3.70 (4H, s, N-CH₂-furan), 3.76 (4H, s, Ar-CH₂-N), 5.01 (4H, s, N-CH₂-O), 5.09 (4H, s, O-CH₂-Ar), 6.26 (2H, d, CH-CH-C), 6.46 (2H, m, CH-CH-CH), 6.82-7.22 (10H, m, Ar-H), 7.65 (2H, m, O-CH-CH).

¹³C-NMR (CDCl₃, δ ppm): 30.8 (CH₂-Ar), 34.1 (CH₂-CO), 53.0 (furan-CH₂-N), 56.3 (Ar-CH₂-N), 66.0 (Ar-CH₂-O), 82.4 (O-CH₂-N), 110.0 (aromatic furan), 111.2 (Ar), 121.1 (Ar), 127.5 (Ar), 128.3 (Ar), 130.4 (Ar), 131.3 (Ar), 139.6 ppm (Ar), 142.1 ppm (aromatic furan), 148.6 (aromatic furan), 155.5 (aromatic furan), 173.6 ppm (C=O).

2.4. Preparation of polybenzoxazines

All the synthesized multifunctional-benzoxazines were cured in a hydraulic press equipped with heating plates. The samples were placed in Teflon molds (15 mm length x 5.5mm width x 1.5 mm thickness) and compression molded (0.25 tn) at 140 °C for 10 min, 180 °C for 60 min, 200 °C for 60 min and 220 °C for 120 min.

2.5. Characterizations

Molecular structure analysis was performed by FTIR and NMR spectrometry. ^1H - and ^{13}C -NMR spectra were registered on a Varian NMR System 400 with a 400MHz frequency. In all cases, 10 mg of sample were dissolved in 0.6 mL of CDCl_3 and tetramethylsilane (TMS) was used as internal standard. FTIR measurements were made in a Perkin-Elmer Spectrometer, model Spectrum One, equipped with accessories for diffuse reflectance (wavenumber range $400\text{--}4000\text{ cm}^{-1}$ and resolution 2 cm^{-1}). A fine powdered sample (5 mg) and KBr (100 mg) was mixed and pressed in order to form a transparent pellet. Liquid samples were dissolved in dichloromethane and suspended on KBr windows.

Dynamic calorimetric analyses were carried out in a Mettler Toledo DSC 821e thermal analyzer. Samples were subjected at $10\text{ }^\circ\text{C/min}$ heating ramp from 30 to $300\text{ }^\circ\text{C}$ under a N_2 gas flow of 20 mL/min .

Viscoelastic behavior was measured using DMTA analyzer (TA Instruments RSA G2). Specimens (15 mm length $\times$ 5.5 mm width $\times$ 1.5 mm thickness) were tested in a 3-point bending mode (5 mm) from 30 to $300\text{ }^\circ\text{C}$ at $3\text{ }^\circ\text{C/min}$, and a fixed frequency of 1 Hz , with a 0.043% strain.

For the thermogravimetric studies (TGA), a Mettler Toledo TGA / SDTA 815e thermal analyzer was used. The analysis was performed under N_2 (50 mL/min) in a working range from 30 to $900\text{ }^\circ\text{C}$ at $10\text{ }^\circ\text{C/min}$. According to the Van Krevelen and Hofytzer equation (Eq. 1) [33], a limiting oxygen index (LOI) was qualitatively estimated.

$$LOI = 17.5 + 0.4(CY) \quad (1)$$

where LOI = limiting oxygen index, and CY = char yield percentage at 850°C in nitrogen. LOI values above 21 allow considering the materials as self-extinguishing and qualified for many flame-retardancy applications [34]. In addition, UL94 vertical position burning test on specimens was performed. In this method, material burning grade is classified as following V-0, V-1, V-2 or unclassified depending on its behavior. This method was performed according to the ASTM-D3801.

3. RESULTS AND DISCUSSION

First, four multi-functional benzoxazine monomers were prepared following a two-step procedure involving: (i) the formation of a phloretic acid-derived monofunctional benzoxazine template with a free carboxylic acid moiety; and (ii) its TMG-assisted esterification with various benzyl bromide (BnBr) compounds. In the first step, two benzoxazines were prepared from phloretic acid and aniline, i.e. PhA-Bz (Scheme 1a), and furfurylamine, i.e. PhF-Bz (Scheme 1b), according to a similar experimental procedure described by Comí *et al.* [23], and Kirubakaran *et al.* [24], respectively. In both cases, the used protocols afforded the pursued benzoxazines in high yields. In a second step, TMG was used to promote an efficient and clean esterification reaction between the carboxylic acid groups present in both benzoxazine templates and commercially available benzyl halides. With the final purpose of obtaining di-, tri- and tetra-functional benzoxazine monomers, α,α' -dibromo-p-xylene (Bn2Br), 1,3,5-tris(bromomethyl)benzene, (Bn3Br), 1,2,4,5-tetrakis(bromomethyl)benzene (Bn4Br) were used. Considering the solubility and reactivity of the reagents (benzoxazine template, BnBr, and TMG), solvents with low environmental impact such as Me-THF and 1,4-dioxane were used to conduct the esterification reaction at room temperature. In all cases, the benzoxazine monomers were efficiently obtained with yields over 90% (Scheme 2), and their chemical structures were verified by FTIR and NMR spectroscopy. FTIR spectra of the four multi-oxazine benzoxazines revealed characteristic absorbance intensities of oxazine ring about 1510, 1228 cm^{-1} and 930 cm^{-1} , as well as of the ester bonds at 1750 cm^{-1} . In addition, for the benzoxazines with furan moieties, the spectra included the following bands: at 1617, 1440, 1010, 763 cm^{-1} assigned to C-O, C-H, C-O and C-H groups, respectively. Regarding ^1H - and ^{13}C -NMR spectra of monomers, the results also showed oxazine characteristic signals, as well as the purity of the resins. As example, Fig. 1 shows the ^1H -NMR spectra of PhF-2Bz and PhA-2Bz monomers, and the signals are identified as follows: i) from 2.5 ppm to 3.0 ppm correspond to methylene-hydrogen; ii) about 5.1 and 4.00 ppm assigned to the methylene O-CH₂-N and methylene Ar-CH₂-N groups, respectively; iii) about 5.2 ppm correspond to methylene-hydrogen between ester and aromatic groups; and iv) from 6.0 to 7.5 ppm associated with the aromatic groups of furan and benzene.

After synthesis, the thermal crosslinking of the four prepared monomers was investigated using DSC Calorimeter and FTIR Spectrometer. Fig. 2 shows the corresponding dynamic calorimetric curves and the data are collected in Table 1. The DSC analysis of aniline-derived difunctional benzoxazine PhA-2Bz revealed a crosslinking exotherm centered at 235 °C, which is characteristic for benzoxazines auto-catalytic curing [35]. Conversely, all the studied furfuryl amine-based systems, i.e. PhF-2Bz, PhF-3Bz, and PhF-4Bz showed a two-peak curing process. This behavior is not only associated with the reactive sites of oxygen, nitrogen and phenoxide *ortho*-position, but also with furan ring reactivity [10,11,36]. According to the ring-opening polymerization mechanisms proposed in the literature[37,38,39], we assume that at high temperatures the 1,3-benzoxazine -O-CH₂-N-bond undergoes a cleavage reaction generating oxazine zwitterion intermediary species. Then, these intermediary species are preferentially attached at the phenoxide *ortho*- and C5-furan ring positions through an electrophilic aromatic substitution reaction to form a furfuryl and Mannich phenolic type crosslinked structure, as shown in Scheme 3. A Mannich Base Phenoxy-type structure can also be formed, it undergoes a rearrangement to a more stable phenolic-type structure above 160°C. In addition, Fig. 2 shows that the curing exotherm onset temperature (T_{onset}) is lower for the furfurylamine-based benzoxazines than for aniline-based benzoxazine exhibiting a ΔT_{onset} of 60 °C. As benzoxazine curing reaction is auto-catalyzed, so the basicity, electronic and steric effects of amine substituents into monomers significantly affect the stability of the nitrogen protonated species. Therefore, we suggest that the furan based protonated species are less thermally stable than the aniline based species, since furan groups contain an electronegative oxygen atom [38]. In addition, note that the T_{onset} decreases when increasing the number of benzoxazines attached to the aromatic core, i.e. PhF-2Bz, PhF-3Bz and PhF-4Bz exhibit T_{onset} of 140, 135 and 120 °C, respectively (Table 1). The lowering in T_{onset} of PhF-4Bz not only is related to the higher concentration of benzoxazine groups per mole of molecule, but also to its close special proximity of oxazine groups per molecule, allowing a great interaction between neighboring rings [37, 39].

Next, the curing behavior of PhA-2Bz and PhF-2Bz was monitored by FTIR (Figs. 3a and b, respectively). Ten spectra were taken during the curing reaction, following the protocol described in experimental section. For PhA-2Bz, spectra from (a) to (j) showed a decrease of the oxazine characteristic absorbance band at 930 cm⁻¹ indicating the ring-opening. As a

consequence of this ring-opening, a progressive decrease of the band at 1510 cm^{-1} attributed to the 1,2,3-tri-substituted aromatic skeleton vibration is also observed, and the apparition of a new band at 1490 cm^{-1} corresponding to the 1,2,3,5-tetra-substituted aromatic skeleton vibration is detected[40]. This is indicative to the formation of the phenolic Mannich bridges. In addition, other vibrations indicative of the crosslinking network are the bands centered at 1650 , and 3380 cm^{-1} .

For the furfurylamine-based difunctional resin (PhF-2Bz), note that from spectra (a) to (j) characteristic bands of oxazine and furan rings exhibit a progressive diminution with time and temperature. Regarding (c) spectrum, the characteristic bands of oxazine ring at 930 and 1510 cm^{-1} decrease, and the bands at 1440 , 1100 and 763 cm^{-1} corresponding to C-O and C-H groups of furan also decrease. This is probably due to oxazine ring opening and to its attachment to the furfuryl C5 position, and to the formation of hydrogen bonds between the furan oxygen and hydroxyl groups (Scheme 3). From (d) spectrum, new overlapping bands appear at 1620 and 1490 cm^{-1} associated with the formation of phenolic Mannich bridges and 1,2,3,5-tetra-substituted benzene rings, respectively. These results confirm the formation of a crosslinked network by Mannich phenolic and furfurylamine bridges, therefore also supports our previous findings by DSC.

The four novel benzoxazine monomers were cured under pressure (0.25 tn) in a hydraulic press, using the temperature program mentioned in the experimental section and $15\text{mm} \times 5.5\text{mm} \times 1.5\text{mm}$ molded specimens were obtained. Fig. 4 shows viscoelastic response of cured multifunctional polybenzoxazine specimens. From the storage modulus data, the crosslinking density of a highly crosslinked polymer can be qualitatively estimated in the rubbery plateau region. In this case, aniline-based polybenzoxazine [Poly(PhA-2Bz)] shows the lowest storage modulus, possibly due to the absence of furfuryl additional crosslinking points. As can also be seen, the Poly(PhA-2Bz) exhibits a slight increase of the storage modulus above $260\text{ }^{\circ}\text{C}$, which can be related to side reactions, usually produced at high temperatures in benzoxazines[37]. For Poly(PhF-2Bz), Poly(PhF-3Bz) and Poly(PhF-4Bz) the increase of crosslinking density should be directly related to the amount of oxazine and furfuryl moieties of their precursors. However, the Poly(PhF-3Bz) has higher storage modulus in rubbery plateau region than Poly(PhF-4Bz). The Poly(PhF-4Bz) viscoelastic

response might be associated with the effect of the curing protocol on the polymerization. Fig. 4 also shows the plots of loss factor ($\tan \delta$) versus temperature. The T_g s of the materials are usually detected as α relaxation peak of the loss factor, and their values are collected in Table 2. Moreover, the width of the $\tan \delta$ curve is a reflex of the heterogeneity of polymers, since it provides information on the distribution of the relaxation times. Therefore, the $\tan \delta$ curves in Fig. 4 show crosslinked networks with relaxation times that occur over a broad range of temperature. This behaviour is due to the high functionality of the polybenzoxazine precursors and to the curing protocol employed, generating networks with highly crosslinked regions and other more limited ones. For example, Poly(PhF-4Bz) exhibits the widest $\tan \delta$ curve, it due to that the benzoxazine precursor (PhF-4Bz) has the highest functionality of oxazine and furan rings.

To determine the effect of the polybenzoxazine chemical structures on the thermal stability and degradation behavior, TGA under nitrogen was studied. Fig. 5 shows the TGA curves and the main data is depicted in Table 2. As can be seen, all polybenzoxazines present thermal stability over 300 °C and have similar degradation trends, exhibiting a single thermal degradation break before their main weight loss stabilizes. This behavior suggests a unique thermal degradation mechanism. Particularly, Poly(PhA-2Bz) exhibits a slight improvement in thermal stability respect to Poly(PhF-2Bz), Poly(PhF-3Bz), and Poly(PhF-4Bz). In addition, it can be seen that the weight loss rate is significantly lower for furan-based polybenzoxazines than aniline-based polybenzoxazine, exhibiting approximately char yields of 58% at 850°C. These results are associated with the functionality and aromatic content in the polymers. However, it is important to note that lower thermal stability in the case of Poly(PhF-4Bz) follows the same trend as in the DMTA analysis (Fig. 4).

In other aspect, Table 2 shows estimated LOI and UL94 test values of the polymers. LOI data were estimated through Eq. 1 with TGA char yield data at 850 °C in nitrogen atmosphere, obtaining 38 and 40 values for aniline-polybenzoxazine and furan-polybenzoxazines, respectively. Regarding UL94 burning test, the four polybenzoxazines exhibited auto-extinguishable characteristics, achieving V-0 grade. Inflammability results indicate good flame retardant behavior for all polybenzoxazines.

3. CONCLUSIONS

Four renewable polybenzoxazine precursors with high functionality of oxazine and furan rings were prepared by tetramethyl guanidine (TMG)-assisted esterification reaction between phloretic acid-benzoxazine based on aniline or furfurylamine and di, tri- and tetra-benzyl bromide compounds. Monomers were obtained with a high purity with yields over 90%. Since the TMG-triggered esterification reaction is an efficient and simple procedure, it might be extended not only to prepare benzoxazine monomers with higher functionality but also to incorporate other functional groups in the benzoxazine structure. Curing analysis of furan-polybenzoxazine precursors confirmed oxazine opening-ring and its attachment to furfuryl C5 and phenoxide-*ortho* positions generating a crosslinked network by phenolic Mannich bridges. The C5 free position of the furfuryl rings not only plays an important role in the curing process but also on the properties of the crosslinked materials. In addition, the reactivity in the thermally induced ring-opening increases with the number of furan and oxazine groups in the molecule. Resultant crosslinked materials revealed good correlation between the number of oxazine rings and the properties of the thermosets. Regarding the furfurylamine-based polybenzoxazines, they showed improved thermal behavior compared to the aniline-based resin, due to the role of furan rings. All materials showed high T_g s, good thermal degradation and stability, and low flammability. These properties are useful in order to use these resins in high-performance and flame-resistance applications.

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Figure captions

Scheme 1. General mechanism of phloretic acid based benzoxazines syntheses: PhA-Bz (a); and PhF-Bz (b).

Scheme 2. General mechanism of multifunctional benzoxazine syntheses: PhA-2Bz; PhF-2Bz; PhF-3Bz; and PhF-4Bz.

Scheme 3. Schematic representation of benzoxazine curing reactions: PhA-2Bz (a) and PhF-2Bz (b).

Figure 1 – ^1H -NMR spectra of benzoxazines: PhA-2Bz (a) and PhF-2Bz (b).

Figure 2 – DSC thermograms of multifunctional benzoxazines.

Figure 3 – Monitoring of curing process by FTIR for (a) PhA-2Bz and (b) PhF-2Bz monomers.

Figure 4 – Viscoelastic behavior of polybenzoxazines by DMTA measurements.

Figure 5 – TGA thermograms of the materials.

TABLES

Table 1 – Crosslinking characteristics and T_g data of the polymers after curing at 140 °C (0.1h), 180 °C (1h), 200 °C (1h) and 220 °C (2h)

Benzoxazine	DSC				T_g (°C)
	T_{onset}^a (°C)	T_{max1}^b (°C)	T_{max2}^b (°C)	ΔH^{oc} (kJ/mol)	$\text{Tan } \delta_{\text{max}}^d$
PhA-2Bz	195	-	233	135,1	245
PhF-2Bz	140	203	242	159,1	250
PhF-3Bz	135	203	239	260,3	260
PhF-4Bz	120	190	230	345,6	240

^a Initial temperature of the crosslinking exotherm (10°C/min).

^b Temperature of the maximum heat release rate (10°C/min).

^c Reaction enthalpy values per mole of benzoxazine.

^d α relaxation peak of the loss factor.

Table 2 – TGA, LOI and UL94 data of the polybenzoxazines

Polybenzoxazine	Nitrogen				LOI ^e	UL94
	T _{5%} ^a	T _{10%} ^b	T _{max} ^c	Char Yield ^d		
Poly(PhA-2Bz)	330	407	437	52	38.3	V-0
Poly(PhF-2Bz)	315	369	400	58	40.7	V-0
Poly(PhF-3Bz)	326	383	471	58	40.7	V-0
Poly(PhF-4Bz)	227	293	439	52	38.3	V-0

^a Temperature (°C) of 5% weight loss.

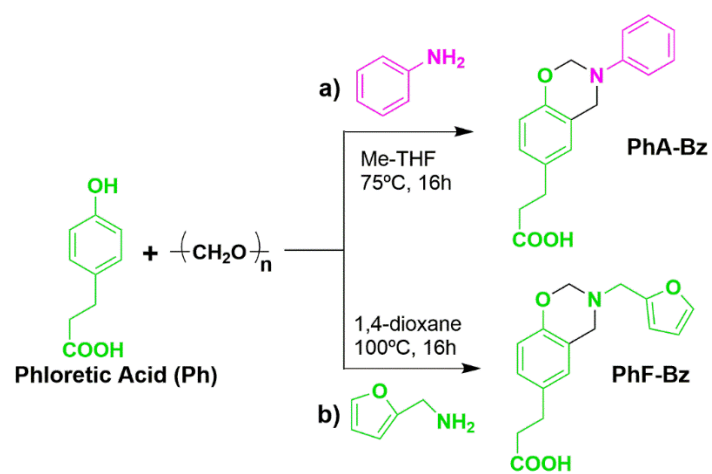
^b Temperature (°C) of 10% weight loss.

^c Temperature of the maximum weight loss rate (°C).

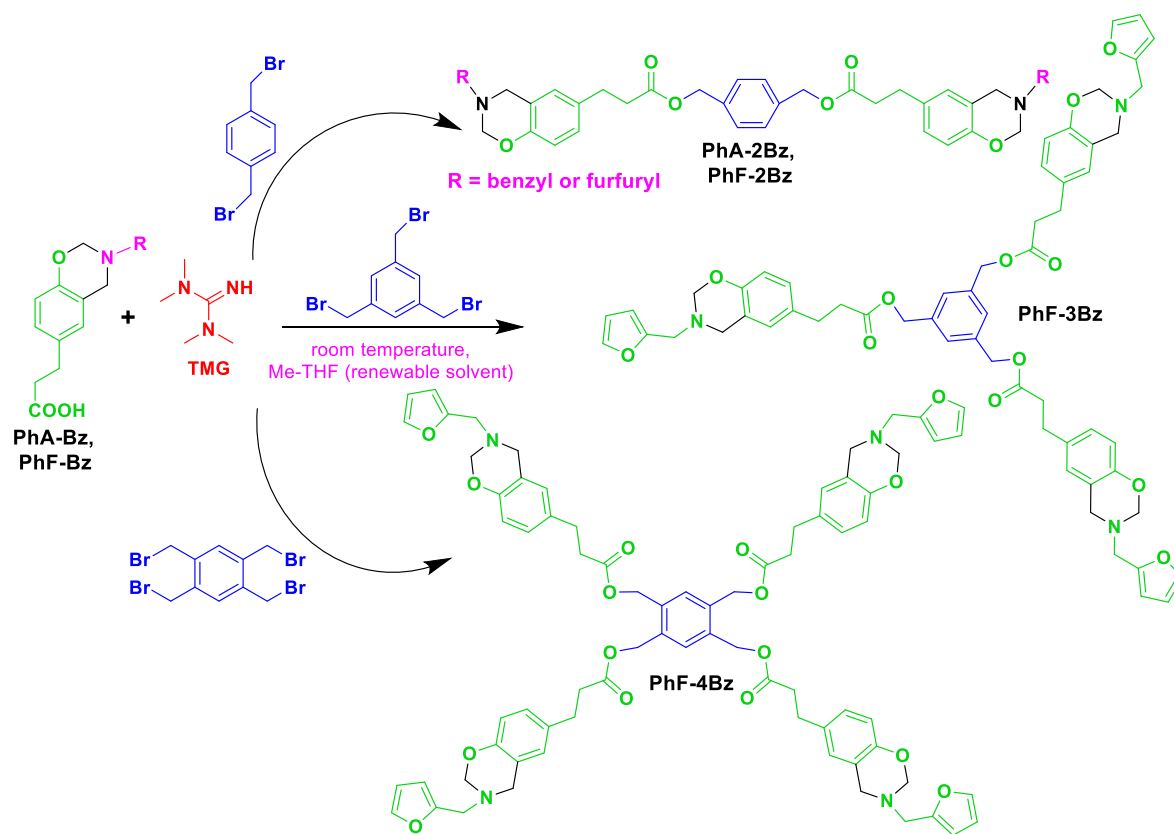
^d Char yield at 850 °C (%).

^e LOI values qualitatively estimated from Van Krevelen equation (Eq. 1).

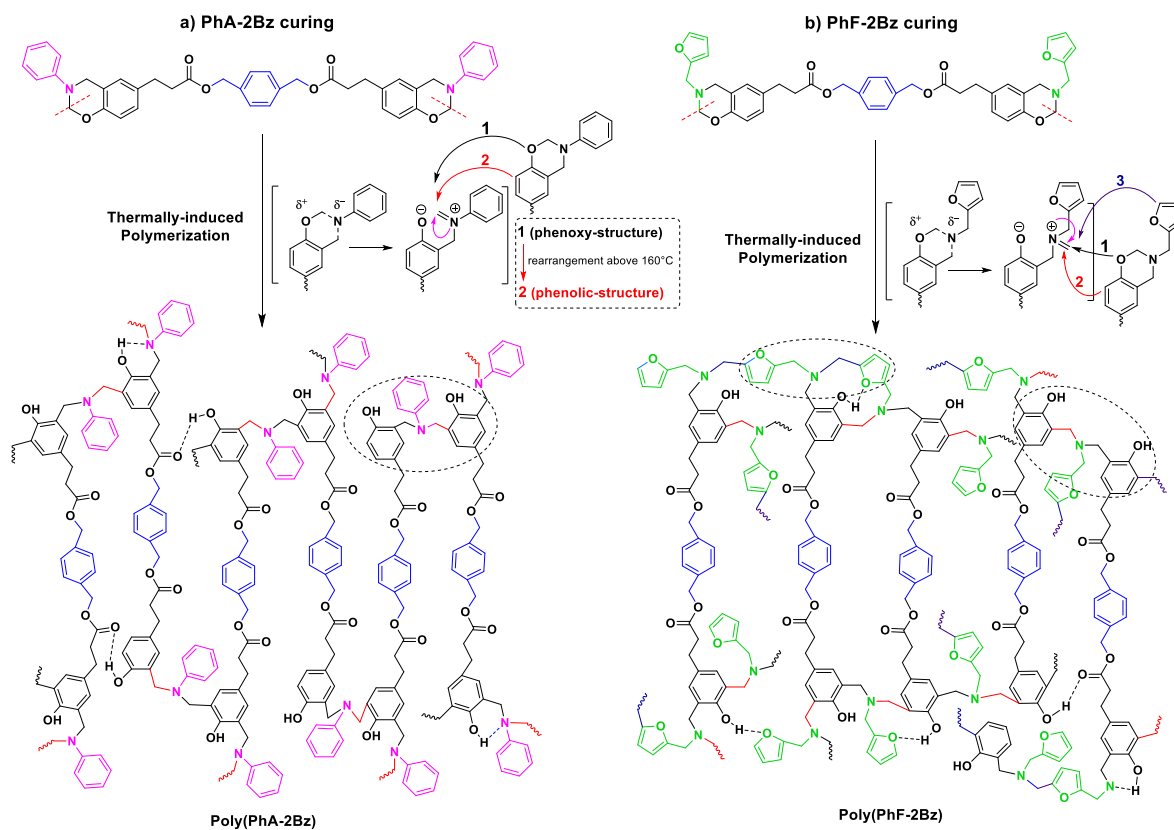
SCHEMES



Scheme 1



Scheme 2



Scheme 3

FIGURES

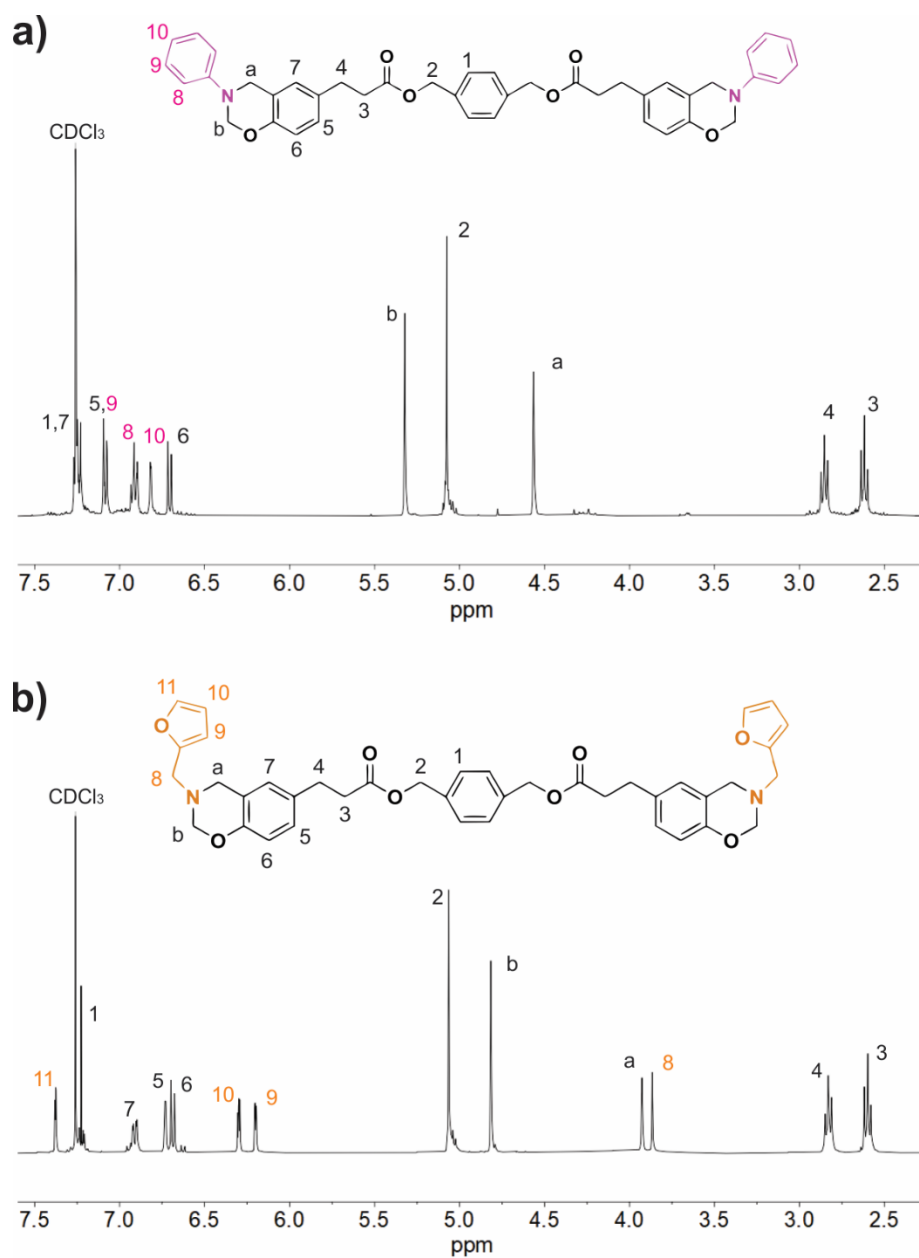


Figure 1

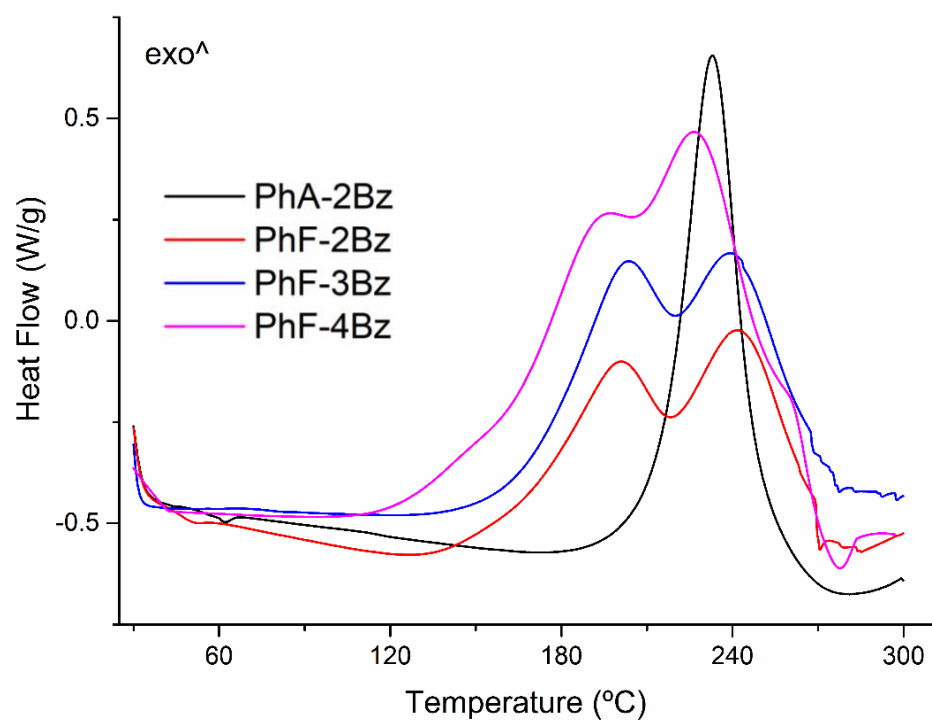


Figure 2

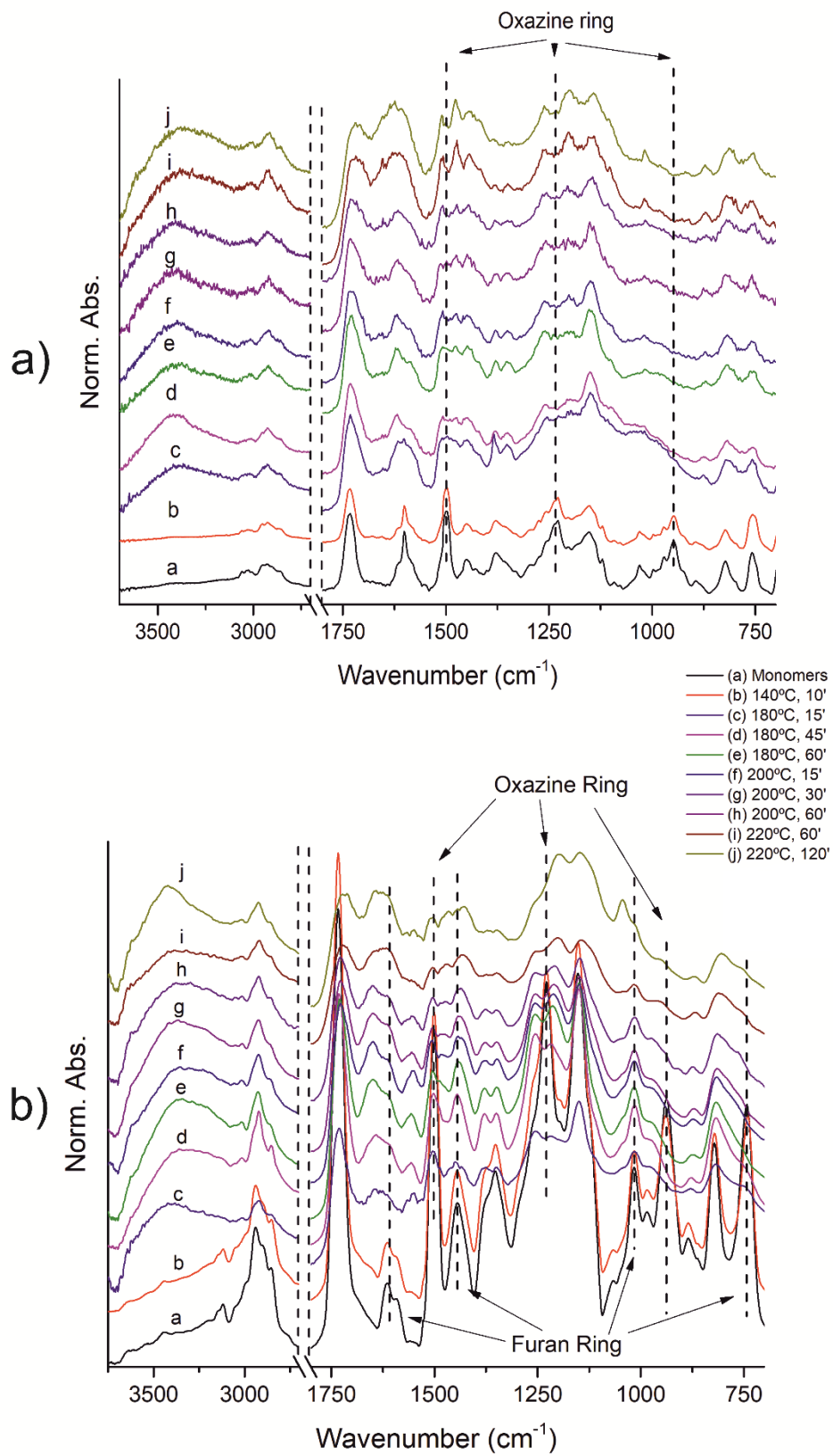


Figure 3

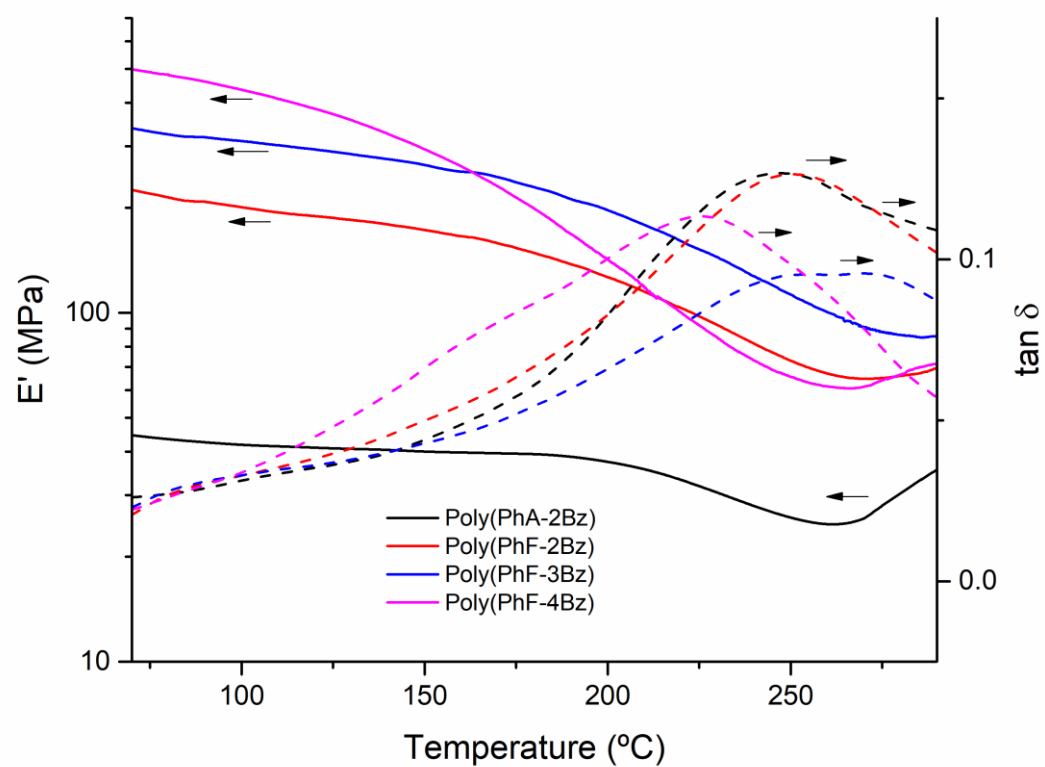


Figure 4

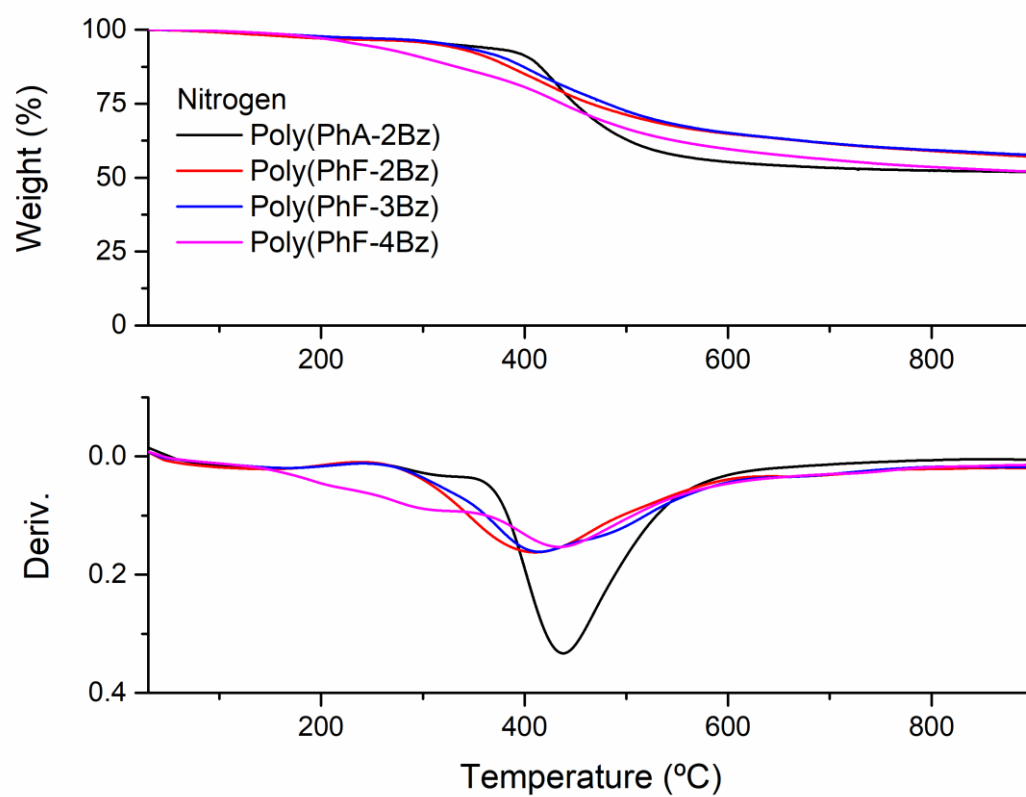


Figure 5

