



Synthesis and characterization of new thermosetting polybenzoxazines with other functional groups in the network

E. Gilbert¹ · M. E. Taverna^{1,2} · M. F. Dieser¹ · G. Morales³ · M. Spontón¹ · D. Estenoz¹

Received: 17 July 2017 / Accepted: 7 March 2018 / Published online: 12 April 2018
© Springer Science+Business Media B.V., part of Springer Nature 2018

Abstract

In this work, novel thermosetting systems of high performance based on multi-functional benzoxazines were developed. First, 3-(2-hydroxyethyl)-3,4-dihydro-2H-1,3-benzoxazine (BzOH) and bis(3-(2-hydroxyethyl)-3,4-dihydro-2H-1,3-benzoxazinyl) isopropane (BzPOH) monomers were synthesized by reaction between phenol or bisphenol A, paraformaldehyde, and ethanolamine. Then, BzOH and BzPOH were functionalized with maleic anhydride using a stoichiometric ratio of oxazine: maleic anhydride (1:1) to produce low molar mass species with carboxylic acid groups, named BzFA and BzPFA. The products were characterized by Nuclear Magnetic Resonance (NMR), Size-Exclusion Chromatography (SEC), and Fourier Transform Infrared Spectroscopy (FTIR). BzFA and BzPFA exhibited weight-average molecular weights of 5000 g.mol⁻¹ and 50,000 g.mol⁻¹, respectively. Mixtures between the new precursors and the conventional benzoxazine (BzBA) derived from bisphenol A and aniline [bis(3-phenyl-3,4-dihydro-2H-1,3-benzoxazinyl) isopropane] were prepared. The curing process was studied by FTIR and Differential Scanning Calorimetry (DSC), and viscoelastic, mechanical, thermal, and morphological properties of the materials were also evaluated. Materials obtained exhibited better thermal, viscoelastic and mechanical properties than conventional polybenzoxazine. Scanning Electron Microscope (SEM) measurements indicated homogeneous material surfaces.

Keywords Benzoxazines · Maleic anhydride · Thermal properties · Thermosets

Introduction

Developments on new advanced polymeric materials for industries such as electronics, aeronautics and aerospace have been actively conducted in recent decades. Materials for these applications must exhibit properties such as high glass transition temperature (T_g), good mechanical behavior, high thermal stability, low water absorption, low internal stress and low dielectric constant [1, 2]. Epoxy and phenolic resins are among the most commonly-used polymers in the cited

industries [3–5]. Polybenzoxazines are a type of high performance phenolic resins exhibiting a very good balance of properties [6]. These thermosetting materials were designed in order to combine thermal and flame retardant properties of phenolic resins with the mechanical performance and molecular design flexibility of advanced epoxy systems [7, 8].

Polybenzoxazines are obtained by opening of 3,4-dihydro-2H-1,3-benzoxazine ring generating phenolic crosslinking structures by Mannich bridge-linked [9, 10]. The benzoxazine ring-opening is produced by an autocatalytic mechanism of phenolic groups formed at the beginning of heating and the process is accelerated due to the acid character of phenolic groups [11]. In spite of this autocatalytic effect, the polymerization of benzoxazines usually requires high temperatures. For this reason, the polymerization process can often overlap with the beginning of degradation [12]. The crosslinking degree of polybenzoxazines is lower than epoxy resins, but polybenzoxazines exhibit higher T_g and Young modulus. The rigidity in the glassy state can be attributed to inter- and intramolecular hydrogen bonds that are sufficiently strong to confine segmental mobility of polybenzoxazine systems [10]. It is

✉ D. Estenoz
destenoz@santafe-conicet.gov.ar

¹ INTEC (Universidad Nacional del Litoral - CONICET), Güemes 3450, (3000) Santa Fe, Argentina

² GPol, Facultad Regional San Francisco, Universidad Tecnológica Nacional, Av. de la Universidad 501, San Francisco, Córdoba, Argentina

³ Centro de Investigación en Química Aplicada (CIQA), Bv. E. Reyna Hemosillo, 140 Saltillo, Coahuila, Mexico

important to note that hydrogen bonds act as a physical crosslinking, and increase the T_g values [11].

Benzoxazine monomers are obtained by a Mannich-type reaction from phenol derivatives, formaldehyde and primary amines [13]. Since polyfunctional benzoxazines lead to crosslinked polymers, the conventional benzoxazine derived from aniline, formaldehyde and bisphenol A (2:4:1), bis-(3-phenyl-3,4-dihydro-2H-1,3 benzoxazinyl) isopropane (BzBA), has been widely studied, and it is commonly used as standard reference [2, 8, 9, 14]. Several studies showed that the use of different monomers [8, 10] and the incorporation of special functional groups [8, 10, 15–18] promotes the development of tailor-made polymers from the point of view of final properties. The main groups incorporated in benzoxazines production in order to improve thermal and mechanical properties are: propargyl [16, 19], allyl [15, 20], nitrile [14], maleimide [21], oxazoline [22], phosphorus [23, 24], trimethoxysilane [4], alcohol [25, 26] and carboxyl [11]. Another attractive alternative to improve the performance of final materials involves the copolymerization or blending between different benzoxazines [27, 28], or with several materials such as epoxies, novolacs, polyurethanes, bismaleimides, polyimides, polystyrene [10, 29–31]. Agag and Takeichi [16] prepared polybenzoxazines derived from monomers containing propargyl groups with improved thermal properties regarding to conventional polybenzoxazines. Besides, they developed polybenzoxazines by copolymerization of allyl containing benzoxazines and conventional BzBA with improved thermomechanical properties [15]. Spontón et al. [23, 24] designed new monomers introducing phenyl phosphine oxide in the structure to increase the T_g , the char yield and the flame retardancy. Kiskan et al. [25] reported the synthesis and characterization and curing at low temperature of two mono- and bifunctional benzoxazine monomers containing oxalcohol groups in the structure. Regarding the incorporation of carboxylic acid groups in benzoxazine synthesis, Andreu et al. [11] obtained materials with good thermal stability, and flame retardancy. Tuzun et al. [32] described the synthesis, characterization, and thermal curing of polyesters containing benzoxazine moieties in the main chain from diacid anhydrides- and diol- containing bisbenzoxazines. Recently, Ishida [20], copolymerized allylamine-terminated oligomeric benzoxazine with maleic anhydride in the presence of a free radical initiator and obtained polymers with good thermal and mechanical properties.

As far as the authors know, publications about the synthesis of benzoxazines with carboxylic groups in their structure using maleic anhydride and its curing with conventional BzBA are not available in the literature.

In this work, the synthesis and characterization of two novel benzoxazines incorporating an acid functional group into the structures were investigated: BzFA and BzPFA. The synthesis of these novel benzoxazines involved the reaction between

phenol or bisphenol A, paraformaldehyde and ethanolamine, to prepare BzOH and BzPOH, respectively. These monomers were functionalized with maleic anhydride in order to obtain two benzoxazine precursors named BzFA and BzPFA. Mixtures of BzBA and new precursors using different weight ratio were also prepared with the aim of developing high performance thermosetting resins. The curing reaction and the material properties were studied by: Fourier Transform Infrared Spectroscopy (FTIR), Differential Scanning Calorimetry (DSC), Thermogravimetric Analysis (TGA), Dynamic Mechanical Thermal Analysis (DMTA), Scanning Electron Microscope (SEM), tensile mechanical and UL-94 test.

Experimental work

Materials

The following chemicals were used: bisphenol A ($\geq 97\%$), purchased from Sigma Aldrich (Saint Louis, USA); aniline ($\geq 99.5\%$), potassium bromide for IR spectroscopy (99.8%), chloroform-D1 for NMR spectroscopy (99.8%) and maleic anhydride ($\geq 99\%$), from Merck (Höhenbrunn, Germany); phenol ($\geq 85\%$), ethanolamine ($\geq 98\%$), paraformaldehyde ($\geq 85\%$), toluene ($\geq 98\%$), *N,N*-dimethylformamide ($\geq 99.8\%$), chloroform ($\geq 99.8\%$), dioxane ($\geq 99\%$), sodium hydroxide ($\geq 97\%$), methylene chloride ($\geq 99.5\%$) ethanol ($\geq 99\%$), and anhydrous magnesium sulphate, from Cicarelli (San Lorenzo, Argentina). All solvents were used as received without further purification.

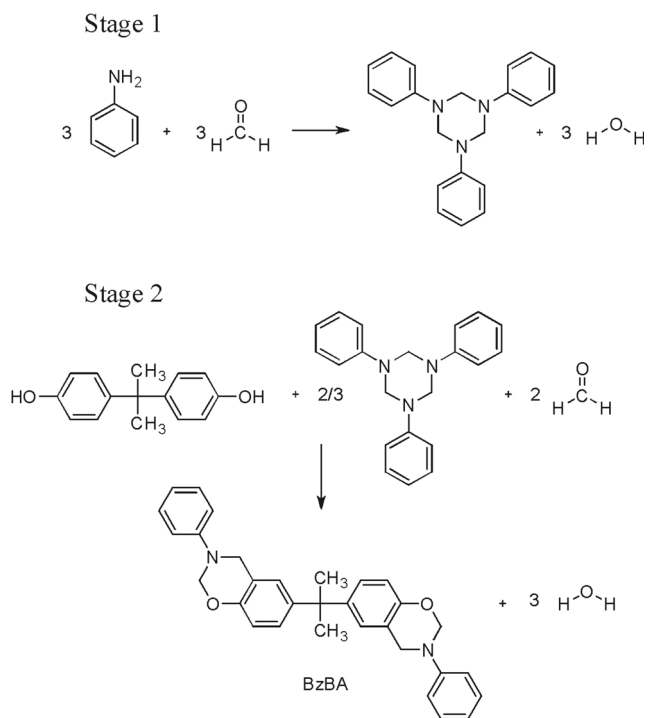
Synthesis and characterization

Synthesis of BzBA

The synthesis of the conventional BzBA was carried out using a two-stage procedure as it is showed in Scheme 1 [33].

First stage: preparation of 1,3,5-Triphenylhexahydro-1,3,5-Triazine In a first stage, 1,3,5-triphenylhexahydro-1,3,5-triazine was synthesized (Scheme 1). To this effect, aniline (93.01 g, 1 mol) and paraformaldehyde (30.03 g, 1 mol) were added into a 250 mL two-necked round bottom flask equipped with a magnetic stirrer. The mixture was heated at 100 °C, and 70 mL of toluene were added under continuous agitation for 2 h. The solution was cooled and the precipitate was filtrated and washed three times with cold toluene. The product was dried at 60 °C.

Second stage: preparation of bis(3-phenyl-3,4-dihydro-2H-1,3benzoxazinyl) isopropane (BzBA) monomer To obtain the BzBA monomer (Scheme 1), 1,3,5-triphenylhexahydro-1,3,5-triazine (15.01 g, 0.047 mol), bisphenol A (16.41 g, 0.072 mol)



Scheme 1 Synthesis of BzBA

and paraformaldehyde (4.33 g, 0.144 mol) were fed into a 250 mL reactor provided with mechanical stirrer. To minimize the amount of oligomers generated during the reaction, an extraction process using sodium hydroxide was carried out. During this process, the mixture was cooled, dissolved in methylene chloride and washed three times with a sodium hydroxide solution at 0.1 mol. L⁻¹. The organic phase was dried over anhydrous magnesium sulphate and concentrated under reduced pressure. To verify its purity, the product was analyzed by NMR and FTIR.

FTIR (KBr, cm⁻¹): 3420 (O-H st), 2960 (-CH₂ st), 1490 (C-C Arst), 1228 (C-O-C st asymmetric), 935 (N-C-O st), 752 (C-N st).

¹H NMR (CDCl₃/TMS, δ (ppm)): 7.32 (m, 2H, Ar), 7.15 (d, 4H, Ar), 6.90 (m, 6H, Ar), 6.86 (s, 2H, Ar), 6.74 (d, 2H, Ar), 5.28 (s, 4H, O-CH₂-N), 4.66 (s, 4H, Ar-CH₂-N), 1.63 (s, 6H, C-CH₃).

¹³C NMR (CDCl₃, δ (ppm)): 152.5, 149.0, 143.5, 129.1, 126.5, 124.9, 121.5, 120.1, 118.2, 116.6, 78.9, 50.7, 41.9, 31.2.

Synthesis of BzFA

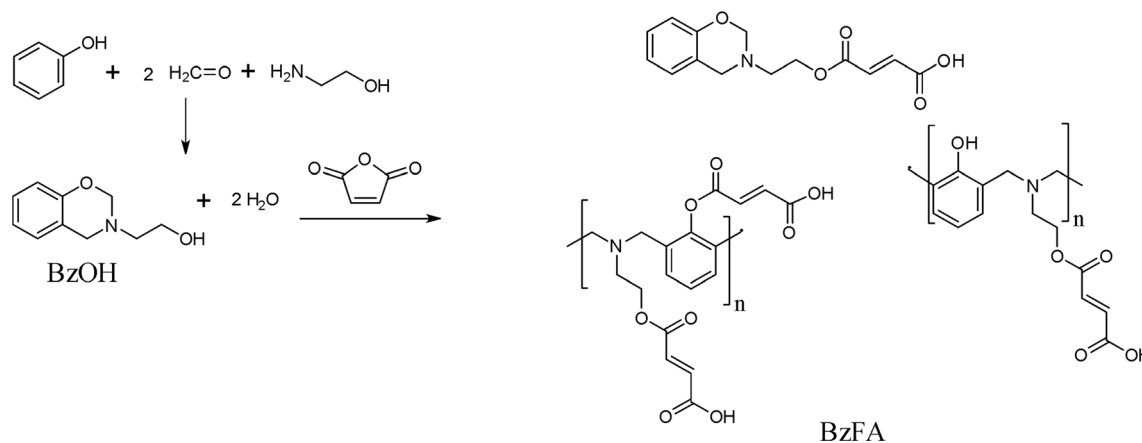
The synthesis of BzFA was conducted in two stages (Scheme 2). Different synthesis strategies were assayed to maximize reaction yield and product purity.

First stage: preparation of 3-(2-hydroxyethyl)-3,4-dihydro-2H-1,3-benzoxazine (BzOH) In a first stage, the BzOH was synthesized by a Mannich-type reaction from phenol, paraformaldehyde and ethanolamine with a molar ratio of 1:2:1 (Scheme 2). Different procedures of reagent addition as well as bulk and solution reactions were assessed. For monomer extraction, various methods were tested modifying the alkali concentration and type of salt. In what follows, the reaction conditions chosen according to the yield and the obtained purity are described.

Paraformaldehyde (6.81 g, 0.227 mol) and ethanolamine (6.92 g, 0.113 mol) were added to a 250 mL reactor provided with mechanical stirring at 235 rpm, and the mixture was heated at 60 °C for 1 h. Then, phenol (10.60 g, 0.113 mol) was incorporated and the reaction was carried out at 90 °C. Total reaction time was 3.5 h. In order to minimize the amount of oligomers formed during the reaction, an extraction process with a sodium hydroxide as explained before solution was carried out.

FTIR (KBr, cm⁻¹): 3420 (O-H st), 2960 (-CH₂ st), 2860 (aliphatic C-H st), 1490 (C-C Ar st), 1260 (C-O-C st asymmetric), 1060 (C-O-C st symmetric), 935 (N-C-O st), 752 (C-N st).

¹H NMR (CDCl₃, δ (ppm)): 7.49–6.61 (m, 4H, Aromatics), 4.81 (s, 2H, O-CH₂-N), 3.93 (s, 2H, Ar-CH₂-N), 3.62 (t, 2H,



Scheme 2 Synthesis of BzOH and BzFA

$\text{CH}_2\text{-CH}_2\text{-OH}$); 2.81 (t, 2H, $\text{N-CH}_2\text{-CH}_2$); 2.62 (s, 1H, $\text{CH}_2\text{-OH}$).

Second stage: preparation of BzFA The BzFA was synthesized from the BzOH with maleic anhydride in a stoichiometric ratio of oxazine: maleic anhydride (Scheme 2). Several reactions were carried out at different temperatures (5, 30 and 75 °C) using different solvents (chloroform and dioxane) in order to study their effect on the yield. No significant differences in yield were observed.

The selected reaction was finally carried out in a reactor with magnetic stirring under inert conditions at 30 °C for 4 h using chloroform as solvent. The recipe included dry chloroform (30 mL), BzOH (10.03 g, 0.056 mol) and maleic anhydride (5.49 g, 0.056 mol). The product was filtered and dried under vacuum. Note that the reaction generates a mixture of benzoxazine compounds named BzFA (Scheme 2).

FTIR (KBr, cm^{-1}): 3420 (O-H st), 2960 ($-\text{CH}_2$ st), 1710 (C=O st), 1615 (C=C st), 1500 (C-C Ar st), 1260 (C-O-C st asymmetric), 1060 (C-O-C st symmetric), 865 (C-N-C st).

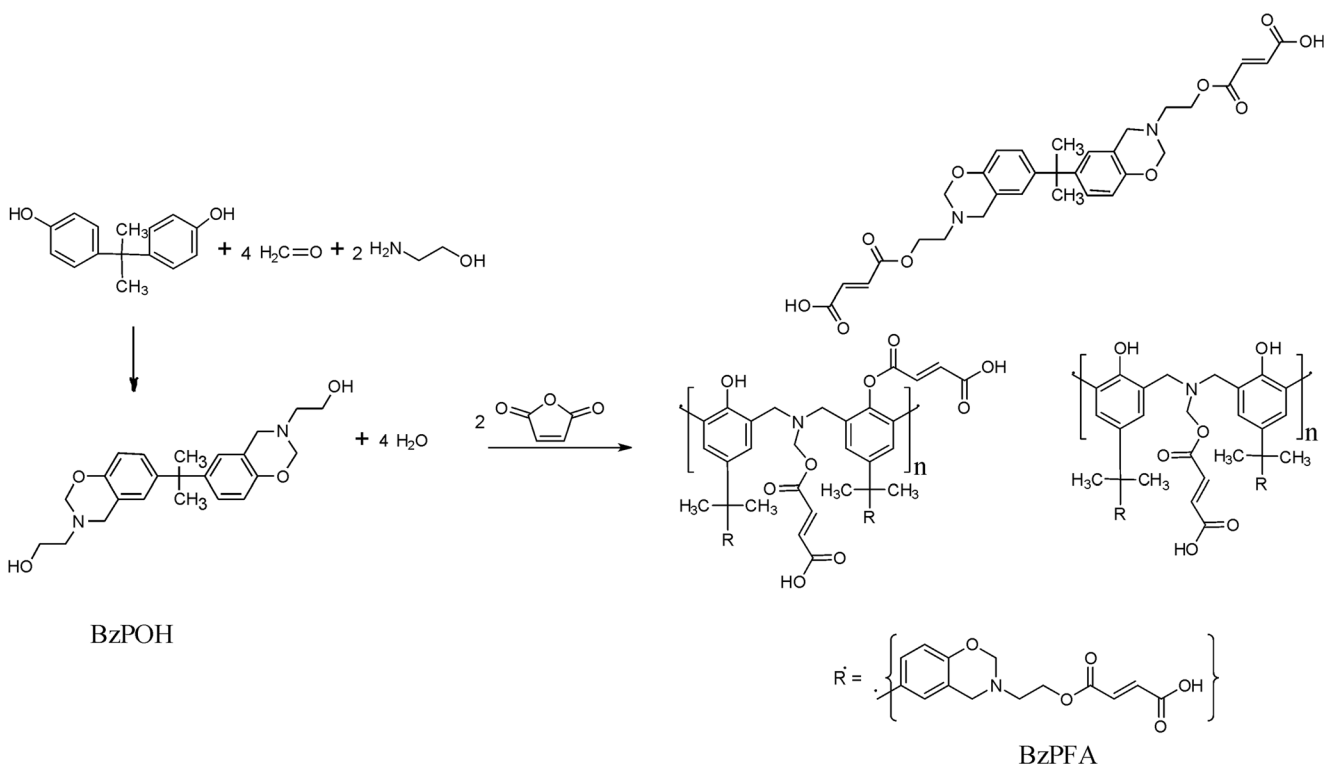
$^1\text{H NMR}$ (CDCl_3), δ (ppm): 10.31 (C(O)-OH); 7.51–6.64 (Aromatics); 6.13 (C-CH-C); 4.82 (O- $\text{CH}_2\text{-N}$); 3.95 (Ar- $\text{CH}_2\text{-N}$); 3.61 ($\text{CH}_2\text{-CH}_2\text{-O}$); 2.83 (N- $\text{CH}_2\text{-CH}_2$).

Synthesis of BzPFA

The two-stage procedure for the synthesis of BzPFA is described (Scheme 3).

First stage: preparation of bis(3-phenyl-3,4-dihydro-2H-1,3benzoxazinyl) isopropane (BzPOH) monomer BzPOH was synthesized from bisphenol A, paraformaldehyde and ethanolamine in a molar ratio of 1:4:2 (Scheme 3). Different reactions were carried out both in bulk as in solution, and using two types of solvents (chloroform and dioxane). Additionally, several extraction processes were performed varying sodium hydroxide concentration. This experimental study aimed at selecting the reaction conditions in order to maximize yield and reduce oligomer content.

The selected bulk process involved the reaction between paraformaldehyde (7.01 g, 0.23 mol) and ethanolamine (7.08 g, 0.116 mol) in a 250 mL reactor provided with mechanical stirring. The reaction was carried out at 60 °C during 1.15 h. Then, bisphenol A (13.24 g, 0.058 mol) dissolved in dioxane (5 mL) was added and the temperature was increased to 90 °C. Total reaction time was 3 h. To minimize the amount of oligomers formed during the reaction, an extraction process, as described before was carried out.



Scheme 3 Synthesis of BzPOH and BzPFA

FTIR (KBr, cm^{-1}): 3420 (O-H st), 2960 ($-\text{CH}_2$ st), 2860 (aliphatic C-H st), 1500 (C-C Ar st), 1230 (C-O-C st asymmetric), 1060 (C-O-C st symmetric), 935 (N-C-O st), 752 (C-N st).

$^1\text{H NMR}$ (CDCl_3 , δ (ppm)): 7.08–6.61 (m, 8H, Aromatics), 4.86 (s, 2H, O- CH_2 -N), 3.92 (s, 2H, Ar- CH_2 -N), 3.65 (t, 2H, CH_2 - CH_2 -OH), 2.86 (t, 2H, N- CH_2 - CH_2), 2.61 (s, 1H, CH_2 -OH), 1.56 (s, 6H, C- CH_3).

Second stage: preparation of BzPFA BzPFA was synthesized from BzPOH and maleic anhydride in a stoichiometric ratio of oxazine: maleic anhydride (Scheme 3). Reactions were carried out using different solvents (chloroform and dioxane). No significant differences in yields were observed.

A three-necked flask of 100 mL equipped with magnetic stirring under inert conditions was used; BzPOH (10.36 g, 0.026 mol) and dry dioxane (10 mL) were added. Then maleic anhydride (5.09 g, 0.052 mol) dissolved in dry dioxane (10 mL) was added dropwise using a syringe. The reaction was carried out at 30 °C for 2.5 h. Finally, the obtained product was filtered and dried under vacuum. As in the synthesis of BzFA, during the preparation of BzPFA, a mixture of benzoxazine compounds was generated (Scheme 3).

FTIR (KBr, cm^{-1}): 3420 (O-H st), 2960 ($-\text{CH}_2$ st), 1710 (C=O st), 1615 (C=C st), 1500 (C-C Ar st), 1260 (C-O-C st asymmetric), 1060 (C-O-C st symmetric), 865 (C-N-C st).

$^1\text{H NMR}$ (CDCl_3 , δ (ppm)): 10.31 (C(O)-OH), 7.18–6.49 (Aromatics), 6.34 (C-CH-C), 4.82 (O- CH_2 -N); 3.91 (Ar- CH_2 -N), 3.75 (CH_2 - CH_2 -O), 2.91 (N- CH_2 - CH_2), 1.59 (C- CH_3).

Crosslinking reactions

BzBA:BzFA and BzBA:BzPFA mixtures were prepared by dissolution of the precursors using different weight ratios (60:40 or 40:60). To prepare the BzBA:BzFA (60:40 weight ratio) mixture; 9.2 g of BzBA monomer, 25 mL dichloromethane, 6.1 g of BzFA and 15 mL of ethanol were added to a 50 mL flask. Similarly,

BzBA:BzPFA 40:60 mixture, was prepared from 6.1 g of BzBA dissolved in 20 mL of methylene chloride, and 9.2 g of BzPFA dissolved in 25 mL of ethanol. Then, all solutions were mixed by sonication during 3 h and evaporated at room temperature under vacuum. In all cases, a yellowish powder was obtained.

Curing reactions of BzBA, BzFA, BzPFA and their mixtures were monitored by dynamic DSC using a heating rate of 10 °C.min $^{-1}$ with a temperature range of 30–350 °C. Since the curing reaction involves a very complex mechanism including gelation, vitrification, subsequent crosslinking, and formation of three-dimensional networks (Scheme 4), materials were cured following non isothermal curing conditions: 180 °C for 2 h, 200 °C for 1 h, 215 °C for 2 h. Along the curing processes, samples were taken and characterized by FTIR.

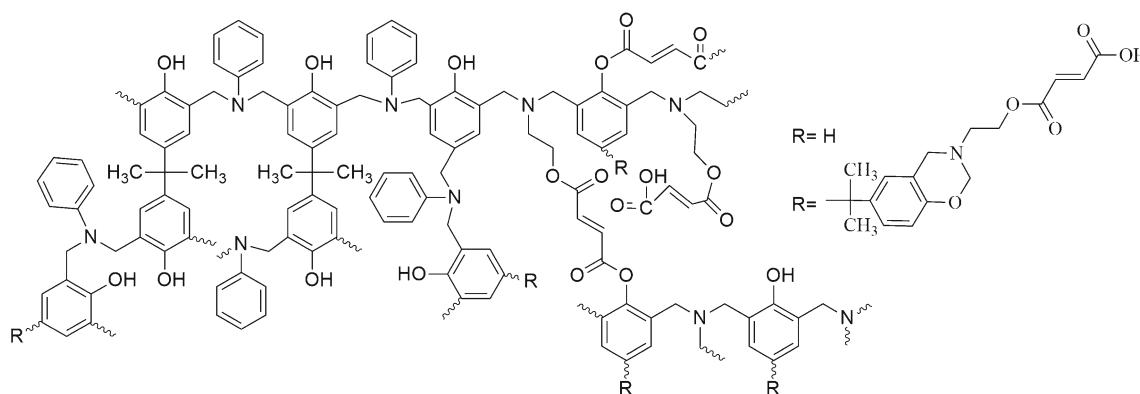
Molded materials (BzBA, BzFA, BzPFA, BzBA:BzFA and BzBA:BzPFA polymers) were prepared with a manual hydraulic press equipped with a water cooled heated platens. Samples were placed in 20 × 10 × 1 mm 3 , 65 × 10 × 1 mm 3 or 70 × 6 × 3 mm 3 molds to analyze viscoelastic, mechanical and thermal properties and morphology.

Instrumentation

FTIR spectra were obtained using a Perkin Elmer FTIR spectrophotometer model Spectrum One with accessories for transmission. For the analysis a fine suspension of the samples was dispersed in KBr, and then pressed to form transparent pellets.

$^1\text{H NMR}$ and $^{13}\text{C NMR}$ were registered on a Bruker 300 Ultrashield (300 MHz) NMR spectrometer with Fourier transform.

Weight-average molecular weights were determined using a Waters SEC device equipped with a Waters 1525 pump, a Shodex KD-803 column (8 × 300 mm) and a Waters 2412 refractive index detector. *N,N*-dimethylformamide was used as eluent with a flow rate of 1 mL.min $^{-1}$ at 40 °C and



Scheme 4 Crosslinking network of new materials

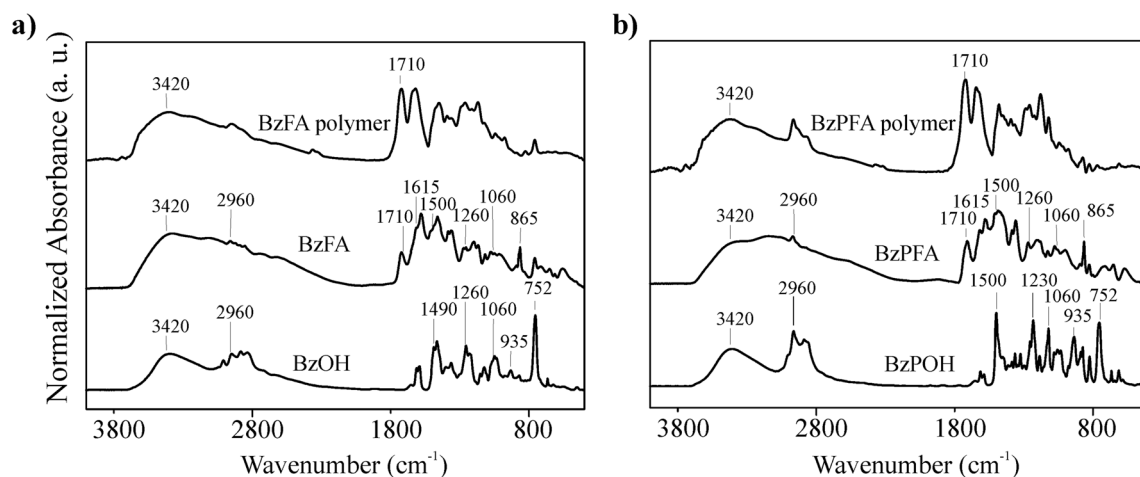


Fig. 1 FTIR spectra of: a) BzOH, BzFA and BzFA-polymer; b) BzPOH, BzPFA and BzPFA-polymer

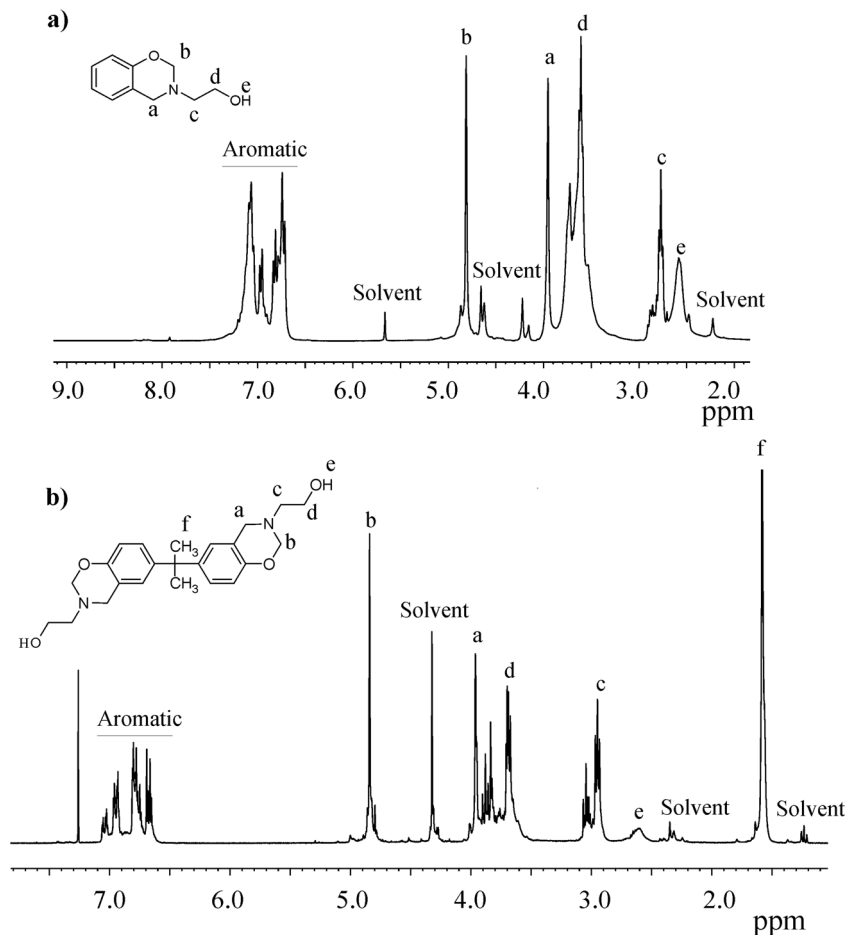
polyethylene glycol (PEG) standards (pegkitwa-07) were used for calibration.

Viscoelastic properties were measured using a dynamic mechanical thermal analysis apparatus (TA Instruments RSA G2). Specimens ($20 \times 10 \times 1 \text{ mm}^3$) were tested in a single cantilever configuration. The

thermal transitions were studied in the range of 30–300 °C at a heating rate of $5 \text{ }^\circ\text{C}\cdot\text{min}^{-1}$ and a fixed frequency of 1 Hz.

Tensile test was carried out in an Instron machine model 3344 Q1469. Tests were performed according to ASTM D638–03. Specimen dimensions were $65 \times 10 \times 1 \text{ mm}^3$.

Fig. 2 ^1H NMR spectra of: a) BzOH and b) BzPOH



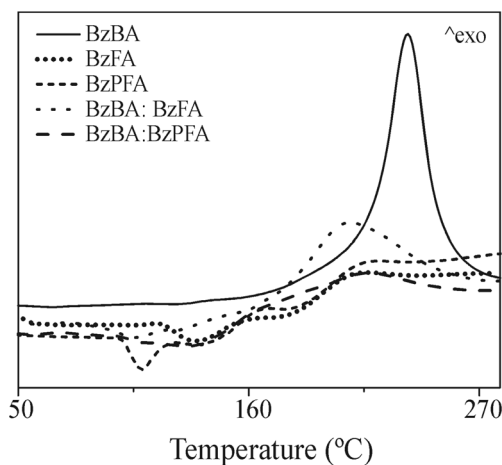


Fig. 3 DSC thermograms of BzBA, BzFA, BzPFA, BzBA:BzFA and BzBA:BzPFA

DSC studies were performed in a Mettler DSC821e thermal analyzer using N_2 as a purge gas ($20 \text{ mL}\cdot\text{min}^{-1}$) at scanning rate of $10 \text{ }^\circ\text{C}\cdot\text{min}^{-1}$. TGA were made in a Mettler TGA/SDTA851e/LF/1100 with N_2 and air as gases ($100 \text{ mL}\cdot\text{min}^{-1}$) at scanning rates of $10 \text{ }^\circ\text{C}\cdot\text{min}^{-1}$.

Flame retardant properties were determined using an UL-94-modified flammability test from Underwriters Laboratories. For this test, samples of $70 \times 6 \times 3 \text{ mm}^3$ were prepared by molding.

Morphologies of sample surfaces were evaluated by SEM, JEOL model JSM-35C, with digital imaging system, at an activation voltage of 20 kV.

Results and discussion

As it was explained before, the syntheses of BzFA and BzPFA were carried out in two stages. In the first stage, the benzoxazine precursors (BzOH and BzPOH) were

obtained. Firstly, the primary amine and paraformaldehyde react to form *N,N*-dihydroxyethanolamine. Then, the *N,N*-dihydroxyethanolamine reacts with the ortho-position of phenol or bisphenol A releasing a water molecule. Finally, the compound is cyclized releasing another water molecule. The average molecular weights obtained by SEC of BzOH and BzPOH confirmed the formation of oligomeric species during the synthesis by reaction between the monomer and the phenol derivatives. The oligomer formation is associated to the basicity of ethanolamine, the alcohol groups in the structure and the presence of impurities that promote the ring opening at lower temperature. In order to purify the monomers, different extraction procedures were carried out by varying the type and concentration of alkali or salts. The maximum yield (up to 85%) was obtained using a $0.1 \text{ mol}\cdot\text{L}^{-1}$ sodium hydroxide solution.

In a second stage, the reaction between BzOH or BzPOH with maleic anhydride enabled to incorporate carboxylic acid groups in the benzoxazine precursors producing BzFA and BzPFA species, respectively.

Figure 1 shows the IR spectra of BzOH, BzFA, BzFA-polymer (Fig. 1a) and BzPOH, BzPFA, BzPFA-polymer (Fig. 1b). In all spectra the absorbance intensities at 3420 and 2960 cm^{-1} are attributed to $-\text{OH}$ and CH_2 groups, respectively. The absorption band corresponding to oxazine ring (935 cm^{-1}) is observed in BzOH and BzPOH spectra. It can be observed that the band at 935 cm^{-1} in BzFA and BzPFA is negligible suggesting the opening of oxazine ring of BzOH and BzPOH in accordance to the results reported by Ishida [20]. In addition, the presence of bands at 1615 and 1710 cm^{-1} attributed to carboxylic acid and ester groups, respectively, confirms the incorporation of maleic anhydride.

The ^1H NMR spectra of BzOH and BzPOH are shown in Fig. 2. The BzOH and BzPOH spectra show signals at around 7.49 and 6.61 ppm corresponding to aromatic protons,

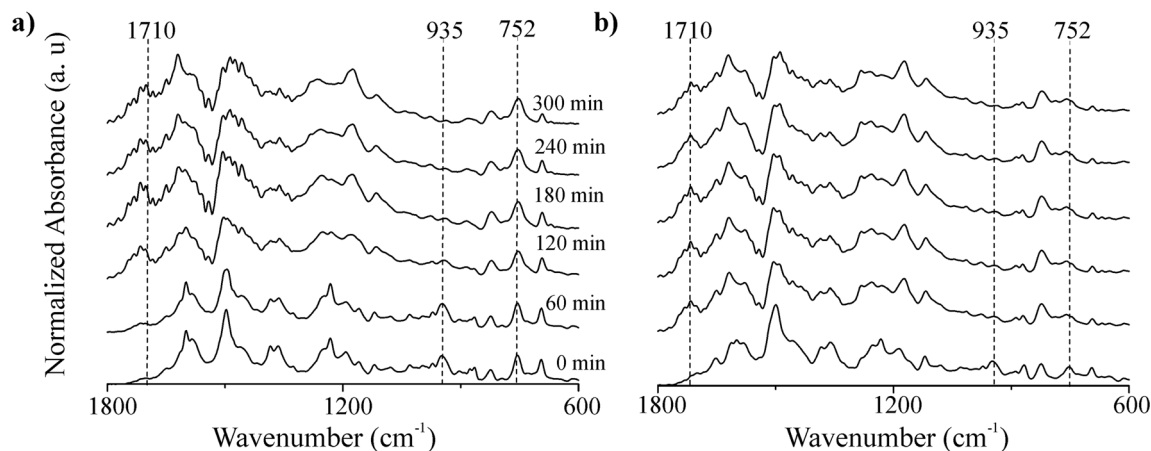


Fig. 4 Monitoring of curing process by FTIR of: a) BzBA:BzFA; and b) BzBA:BzPFA

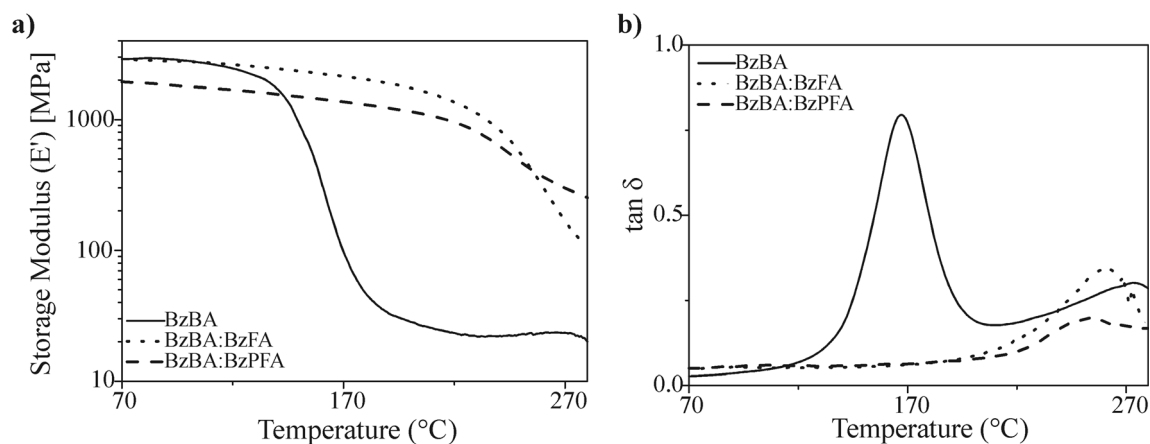


Fig. 5 DMTA measurements: a) Storage modulus (E'); and b) $\tan \delta$

and singlets at 4.81 and 3.92 ppm assigned to the $O-CH_2-N$ and $Ar-CH_2-N$ of oxazine ring, respectively. Also, signals at 3.62 and 2.86 ppm corresponding to the hydrogen triplets of the aliphatic methylene groups can be observed. The hydrogen singlet of hydroxyl group is also observed in both spectra. Signals obtained from BzFA and BzPFA spectra are summarized in Experimental Work Section. In spite of the difficulty to interpret BzFA and BzPFA spectra, a signal at 10.3 ppm could be identified that it is associated to carboxylic acid protons. The weight-average molecular weight (\overline{M}_w) of BzFA and BzPFA measured by SEC were 5000 and 50,000 $g \cdot mol^{-1}$, respectively, confirming the formation of low molar mass species due to the high reactivity of the acid groups formed in the second stage of the reaction.

Figure 3 shows the DSC thermograms of BzBA, BzFA, BzPFA, BzBA:BzFA and BzBA:BzPFA. The BzBA exotherm exhibits a maximum at 240 °C. This indicates that the dominant mechanism of curing is the ring opening

reaction, leading to the formation of the three-dimensional network of phenolic Mannich bridges [4]. BzFA and BzPFA present T_g s around 100 °C, and residual enthalpies start at 135 °C and 140 °C, respectively. Both compounds exhibit more than one chemical curing mechanism. The first curing process could be due to the ring opening of the residual oxazine, while the second to esterification reactions between acid groups, and between acid groups with phenolic groups [5, 20, 34]. The BzBA:BzFA and BzBA:BzPFA mixtures start curing at a lower temperature than the conventional BzBA with maximum (T_{max}) centered in 210 °C and 220 °C, respectively. The results reveal the catalytic effect of carboxylic acid groups and phenolic groups. The multiple curing mechanisms could involve the oxazine ring opening, and the esterification between carboxylic acid groups, and acid and phenolic groups present (Scheme 4). In both cases, the curing mechanism leads to the formation of the

Table 1 Properties of cured materials

Samples	Weight ratio (wt%)	DSC		DMTA			Tensile -Test		
		T_{onset}^a (°C)	T_{max}^b (°C)	T_g^c (°C)	$[E']^d$ (Pa)	Young Module (GPa)	Tensile Strength (MPa)	Elongation at break (%)	
									$[\tan \delta]$ (°C)
BzBA	100	160	240	167	150	28	1.39	29.3	2.62
BzFA	100	135	215	–	–	–	–	–	–
BzPFA	100	140	220	–	–	–	–	–	–
BzBA:BzFA	60:40	100	210	260	247	83	–	–	–
BzBA:BzPFA	60:40	130	220	253	245	175	1.43	41.08	2.51

^a Initial temperature of the crosslinking exotherm

^b Temperature of the maximum heat release rate

^c Glass transition temperature obtained by DMTA

^d E' estimated from the plateau of the elastic modulus in the rubbery state

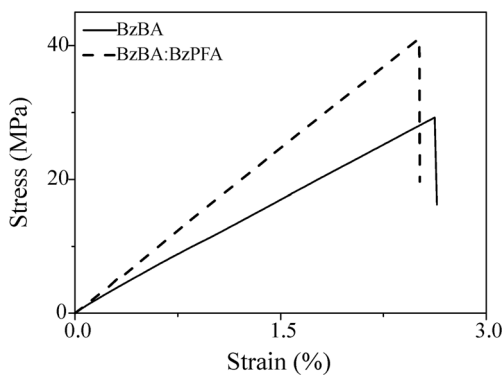


Fig. 6 Tensile test for BzBA and BzBA:BzPFA

three-dimensional network of phenolic Mannich bridges and ester bridges.

In Fig. 4 the FTIR spectra of mixtures BzBA:BzFA (Fig. 4 a) and BzBA:BzPFA (Fig. 4 b) are shown. The band at 752 cm^{-1} corresponding to C-N stretching is used to normalize the spectra [23, 27]. For the two systems a progressive diminution of the characteristic band corresponding to the oxazine ring can be noted along the curing. The increment of the band at 1710 cm^{-1} in Fig. 1 and Fig. 4 could be associated to esterification between acid groups, and acid groups with phenolic groups.

The viscoelastic behavior of cured benzoxazines as a function of temperature was studied (Fig. 5), from the glassy state to the rubbery plateau of each material. The crosslinking density of the polymers can be estimated from the plateau of the elastic modulus in the rubbery state. However, this theory is strictly valid only for lightly crosslinked materials and for this reason was used only to make qualitative comparisons of the crosslinking degree. Note that the DMTA analysis of BzFA and BzPFA polymers could not be evaluated due to the high fragility of samples. As it can be seen in Fig. 5, the crosslinking density of benzoxazine mixtures (BzBA:BzFA and BzBA:BzPFA) is higher than that of BzBA (Fig. 5a).

Tg of materials can be estimated from the maximum of $\tan \delta$ or from the loss module (E''). Table 1 shows Tg values obtained by both measurements. The results indicate that the Tg of the mixtures (BzBA:BzFA and BzBA:BzPFA) are higher than that of BzBA. This can be explained by the lower segmental mobility associated to ester bonds and a higher amount of hydrogen bridge bonds in the mixtures [5, 11, 20, 35].

The results of tensile test (Fig. 6 and Table 1) reveal a linear elastic behavior and an increase of Young module for BzBA:BzPFA samples. This result can be associated to the network of copolymer crosslinked by ester linkages and hydrogen bridge bonds, conferring greater rigidity to the

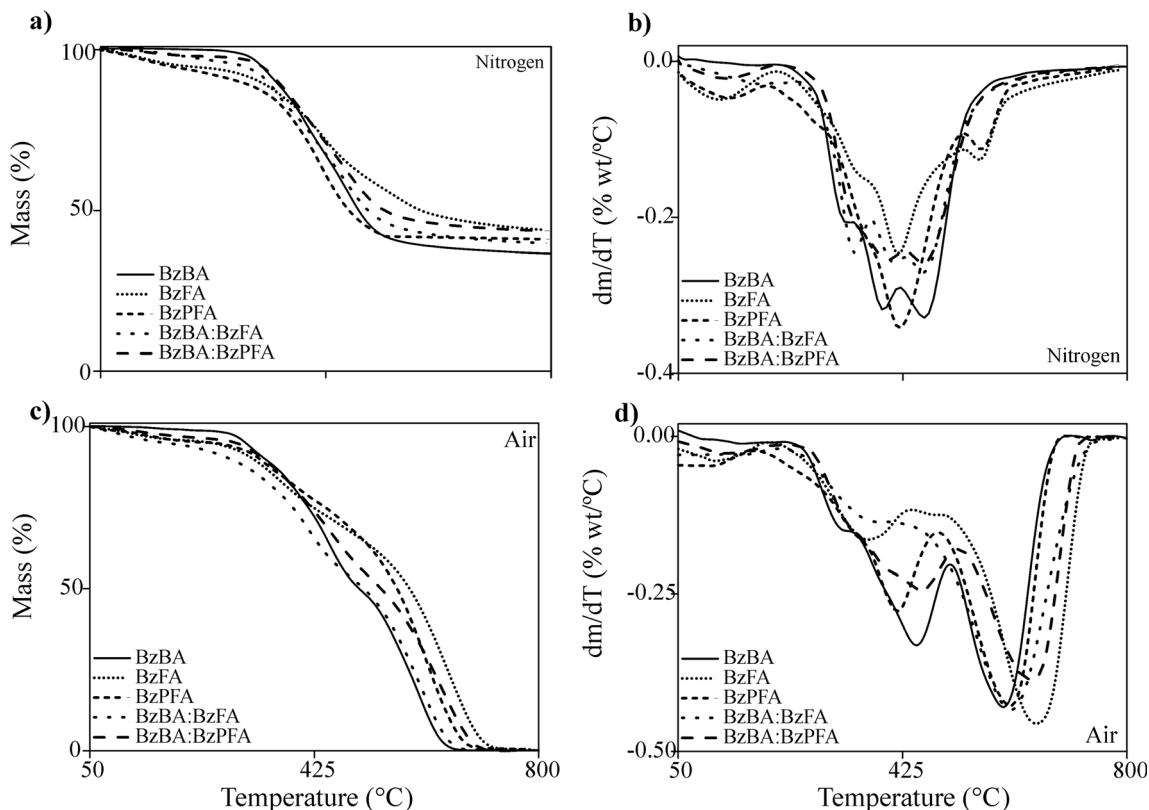


Fig. 7 TGA thermograms and their first derivative of BzBA, BzFA, BzPFA, BzBA:BzFA and BzBA:BzPFA in nitrogen (a) and air (b)

Table 2 Thermogravimetric properties

Samples	TGA								UL-94
	Nitrogen				Air				
	T _{5%} ^a (°C)	T _{50%} ^b (°C)	T _{max} ^c (°C)	Char ^d (%)	T _{5%} ^a (°C)	T _{50%} ^b (°C)	T _{max} ^c (°C)	Char ^d (%)	
BzBA	315	477	390; 460	37	309	499	448; 594	–	V-0
BzFA	186	583	421; 555	44	251	586	366; 651	–	V-0
BzPFA	185	461	421; 554	41	169	508	343; 603	–	V-0
BzBA:BzFA	284	495	414; 461	40	252	562	330; 632	–	V-0
BzBA:BzPFA	315	518	461	44	298	537	397; 641	–	V-0

^a Temperature of 5% weight loss

^b Temperature of 50% weight loss

^c Temperature of the maximum weight loss rate

^d Char yield at 800 °C

material. Accurate measurements for BzBA:BzFA could not be performed due to the presence of microcracks in the samples associated to its preparation.

The thermal stability and degradation behavior of final materials were investigated by TGA under nitrogen and air atmosphere; Fig. 7 and Table 2 summarize the results.

The thermal stability for BzBA, BzFA, BzPFA and mixtures at 5% of degradation could not be compared because BzFA, BzPFA and mixtures are hydrophilic materials and consequently showed weight losses corresponding to moisture content. Similar results were obtained by Kiskan et al. [25]. However, at higher temperatures it can be noted that BzFA, BzPFA and the mixtures present a delayed degradation in comparison to BzBA, and for this reason, the BzBA degradation behavior is improved by the addition of BzFA or BzPFA. As shown in Table 2

and Fig. 7, the char yield under nitrogen atmosphere is 37%, 40% and 44% for BzBA, BzBA:BzFA and BzBA:BzPFA, respectively. Under air atmosphere, the char yield is 0% at 800 °C due to thermoxidative degradation.

The flame retardancy of the materials was evaluated from UL-94 test. The results are presented in Table 2. For all materials, UL-94 test reveals V-0 degree indicating good flame retardancy.

Finally, the morphologies of the materials obtained by SEM are shown in Fig. 8, revealing homogeneous surfaces without phase separation. However, at higher magnifications, a slight roughness can be observed for all materials.

Note that only results for BzBA:BzFA and BzBA: BzPFA mixtures with 60:40 weight ratio are shown due to the better performance obtained in comparison to those with 40:60 weight ratio.

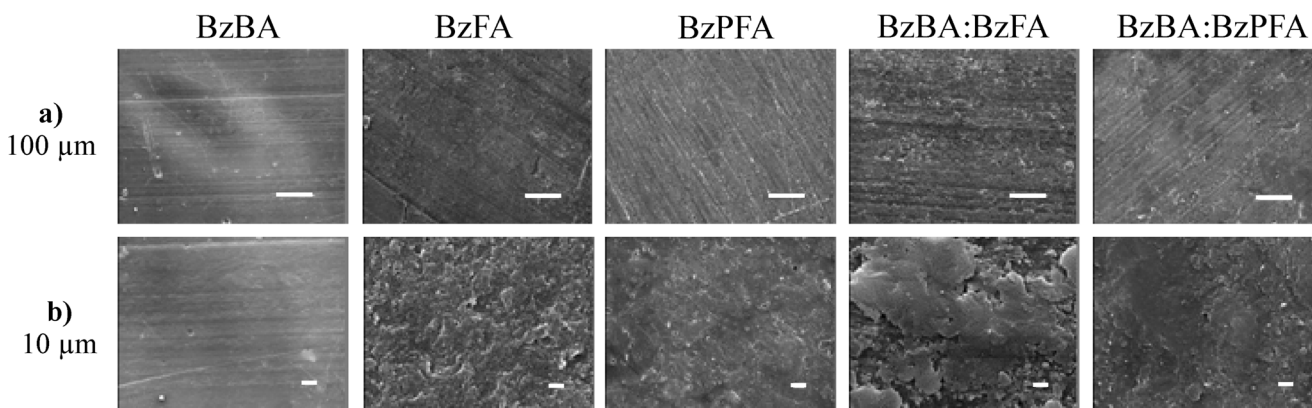


Fig. 8 SEM micrographs of BzBA, BzFA, BzPFA, BzBA:BzFA and BzBA:BzPFA

Conclusions

Two novel benzoxazines (BzFA and BzPFA) with carboxylic acid groups in their structures were synthesized and characterized by SEC, FTIR and ^1H NMR.

The experimental results showed that BzFA and BzPFA exhibited more than one chemical curing mechanism. The curing process included the oxazine ring opening, forming a three-dimensional network of phenolic Mannich bridges and the esterification by condensation between carboxylic acid groups, and carboxylic acid and phenolic groups.

Materials obtained from BzBA:BzFA and BzBA:BzPFA mixtures showed better thermal, viscoelastic and mechanical properties in comparison with the conventional BzBA polymer. These results can be associated to the crosslinked network by ester linkages that promote a high material rigidity. The results of UL-94 test, showed good flame retardant properties. Finally, materials exhibited homogeneous surfaces.

Acknowledgments The authors are grateful to the Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET), Universidad Nacional del Litoral (UNL), Universidad Tecnológica Nacional (UTN), and Agencia Nacional de Promoción Científica y Tecnológica (ANPCyT) for the financial support.

Compliance with ethical standards

Conflicts of interest The authors declare that they have no conflicts of interest.

References

- Li S, Yang C, Li C, Yan S (2017) Synthesis, characterization of new bisphenol-based benzoxazines and the thermal properties of their polymers. *J Therm Anal Calorim* 128:1711–1717. <https://doi.org/10.1007/s10973-017-6099-5>
- Allen DJ, Ishida H (2006) Physical and mechanical properties of flexible polybenzoxazine resins: Effect of aliphatic diamine chain length. *J Appl Polym Sci* 101:2798–2809. <https://doi.org/10.1002/app.22501>
- Fonseca Costa e Silva S, Machado Araújo A, Bittencourt E (2015) Effect of the fiber orientation relatively to the plasma flow direction in the ablation process of a carbon-phenolic composite. *J Aerosp Technol Manag* 7:43–52. <https://doi.org/10.5028/jatm.v7i1.437>
- Sponton M, Estenoz D, Lligadas G et al (2012) Synthesis and characterization of a hybrid material based on a trimethoxysilane functionalized benzoxazine. *J Appl Polym Sci* 126:1369–1376. <https://doi.org/10.1002/app.36766>
- Kimura H, Ohtsuka K, Matsumoto A (2011) Curing reaction of bisphenol-A based benzoxazine with cyanate ester resin and the properties of the cured thermosetting resin. *Express Polym Lett* 5: 1113–1122. <https://doi.org/10.3144/expresspolymlett.2011.108>
- Gietl T, Lengersfeld H, Altstädt V (2006) The efficiency of various toughening agents in novel phenolic type thermoset resin systems. *J Mater Sci* 41:8226–8243. <https://doi.org/10.1007/s10853-006-0879-9>
- Zhang L, Wang M, Wu J (2016) Study on an amine-containing benzoxazine: Homo- and copolymerization with epoxy resin. *Express Polym Lett* 10:617–626. <https://doi.org/10.3144/expresspolymlett.2016.56>
- Ishida H, Allen D (1996) Physical and mechanical characterization of near-zero shrinkage polybenzoxazines. *J Polym Sci B Polym Phys* 34:1019–1030. [https://doi.org/10.1002/\(SICI\)1099-0488\(19960430\)34:6<1019::AID-POLB1>3.0.CO;2-T](https://doi.org/10.1002/(SICI)1099-0488(19960430)34:6<1019::AID-POLB1>3.0.CO;2-T)
- Kimura H, Matsumoto A, Ohtsuka K (2008) Studies on new type of phenolic resin — curing reaction of bisphenol-a-based benzoxazine with epoxy resin using latent curing agent and the properties of the cured resin. *J Appl Polym Sci* 109:1248–1256. <https://doi.org/10.1002/app.28279>
- Ghosh NN, Kiskan B, Yagci Y (2007) Polybenzoxazines-new high performance thermosetting resins: synthesis and properties. *Prog Polym Sci* 32:1344–1391. <https://doi.org/10.1016/j.progpolymsci.2007.07.002>
- Andreu R, Reina JA, Ronda JC (2008) Carboxylic acid-containing benzoxazines as efficient catalysts in the thermal polymerization of benzoxazines. *J Polym Sci A Polym Chem*:6091–6101. <https://doi.org/10.1002/pola>
- Ishida H, Ohba S (2005) Synthesis and characterization of maleimide and norbornene functionalized benzoxazines. *Polymer* 46:5588–5595. <https://doi.org/10.1016/j.polymer.2005.04.080>
- Holly W, Cope C (1944) Condensation products of aldehydes and ketones with o-aminobenzyl alcohol and o-hydroxybenzylamine. *J Am Chem Soc* 66:1875–1879. <https://doi.org/10.1021/ja01239a02>
- Brunovska Z, Ishida H (1999) Thermal study on the copolymers of phthalonitrile and phenylnitrile-functional benzoxazines. *J Appl Polym Sci* 73:2937–2949. [https://doi.org/10.1002/\(SICI\)1097-4628\(19990929\)73:14<2937::AID-APP18>3.0.CO;2-E](https://doi.org/10.1002/(SICI)1097-4628(19990929)73:14<2937::AID-APP18>3.0.CO;2-E)
- Agag T, Takeichi T (2003) Synthesis and characterization of novel benzoxazine monomers containing allyl groups and their high performance thermosets. *Macromolecules* 36:6010–6017. <https://doi.org/10.1021/ma021775q>
- Agag T, Takeichi T (2001) Novel benzoxazine monomers containing p-phenyl propargyl ether: polymerization of monomers and properties of polybenzoxazines. *Macromolecules* 34:7257–7263. <https://doi.org/10.1021/ma0107915>
- Ishida H, Low HY (1997) A study on the volumetric expansion of benzoxazine-based phenolic resin. *Macromolecules* 30:1099–1106. <https://doi.org/10.1021/ma960539a>
- Ishida H, Rodriguez Y (1995) Curing kinetics of a new benzoxazine-based phenolic resin by differential scanning calorimetry. *Polymer* 36:3151–3158. [https://doi.org/10.1016/0032-3861\(95\)97878-J](https://doi.org/10.1016/0032-3861(95)97878-J)
- Kiskan B, Yagci Y (2008) Synthesis and characterization of thermally curable polyacetylenes by polymerization of propargyl benzoxazine using rhodium catalyst. *Polymer* 49: 2455–2460. <https://doi.org/10.1016/j.polymer.2008.03.031>
- Liu J, Scott C, Winroth S et al (2015) Copolymers based on telechelic benzoxazine with a reactive main-chain and anhydride: monomer and polymer synthesis, and thermal and mechanical properties of carbon fiber composites. *RSC Adv* 5:16785–16791. <https://doi.org/10.1039/C4RA12086H>
- Takeichi T, Saito Y, Agag T et al (2008) High-performance polymer alloys of polybenzoxazine and bismaleimide. *Polymer* 49:1173–1179. <https://doi.org/10.1016/j.polymer.2008.01.041>
- Cao H, Xu R, Yu D (2008) Synthesis and Characterization of 2-Oxazoline-benzoxazine Compound and its Polymer. *J Appl Polym Sci* 110:1502–1508. <https://doi.org/10.1002/app.27787>
- Sponton M, Ronda JC, Galià M, Cádiz V (2008) Studies on thermal and flame retardant behaviour of mixtures of bis(m-aminophenyl) methylphosphine oxide based benzoxazine and glycidylether or benzoxazine of Bisphenol A. *Polym Degrad Stab* 93:2158–2165. <https://doi.org/10.1016/j.polymdegradstab.2008.08.004>

24. Spontón M, Ronda JC, Galià M, Cádiz V (2009) Development of flame retardant phosphorus- and silicon-containing polybenzoxazines. *Polym Degrad Stab* 94:145–150. <https://doi.org/10.1016/j.polymdegradstab.2008.11.017>
25. Kiskan B, Koz B, Yagci Y (2009) Synthesis and Characterization of Fluid 1,3-Benzoxazine Monomers and Their Thermally Activated Curing. *J Polym Sci A Polym Chem* 47(24):6955–6961. <https://doi.org/10.1002/pola.23735>
26. Kudoh R, Sudo A, Endo T (2010) A Highly Reactive Benzoxazine Monomer, 1-(2-hydroxyethyl)-1,3-Benzoxazine: Activation of Benzoxazine by Neighboring Group Participation of Hydroxyl Group. *Macromolecules* 43(3):1185–1187. <https://doi.org/10.1021/ma902416h>
27. Soto M, Hiller M, Oschkinat H, Koschek K (2016) Multifunctional benzoxazines feature low polymerization temperature and diverse polymer structures. *Polymers* 8:278. <https://doi.org/10.3390/polym8080278>
28. Kumar KSS, Nair CPR, Sadhana R, Ninan KN (2007) Benzoxazine – bismaleimide blends : Curing and thermal properties. *Eur Polym J* 43:5084–5096. <https://doi.org/10.1016/j.eurpolymj.2007.09.012>
29. Gacal B, Cianca L, Agag T et al (2007) Synthesis and characterization of maleimide (co)polymers with pendant benzoxazine groups by photoinduced radical polymerization and their thermal curing. *J Polym Sci A Polym Chem* 45: 2774–2786. <https://doi.org/10.1002/pola.22034>
30. Espinosa M, Galià M, Cádiz V (2004) Novel phosphorilated flame retardant thermosets: epoxy–benzoxazine–novolac systems. *Polymer* 45:6103–6109. <https://doi.org/10.1016/j.polymer.2004.07.002>
31. Rimdusit S, Ishida H (2000) Development of new class of electronic packaging materials based on ternary systems of benzoxazine, epoxy, and phenolic resins. *Polymer* 41:7941–7949. [https://doi.org/10.1016/S0032-3861\(00\)00164-6](https://doi.org/10.1016/S0032-3861(00)00164-6)
32. Tuzun A, Kiskan B, Alemdar N, Erciyes AT, Yagci Y (2010) Benzoxazine Containing Polyester Thermosets with Improved Adhesion and Flexibility. *J Polym Sci A Polym Chem* 48(19): 4279–4284. <https://doi.org/10.1002/pola.24215>
33. Brunovska Z, Liu JP, Ishida H (1999) 1,3,5-Triphenylhexahydro-1, 3,5-triazine - active intermediate and precursor in the novel synthesis of benzoxazine monomers and oligomers. *Macromol Chem Phys* 200:1745–1752. [https://doi.org/10.1002/\(SICI\)1521-3935\(19990701\)200:7<1745::AID-MACP1745>3.0.CO;2-D](https://doi.org/10.1002/(SICI)1521-3935(19990701)200:7<1745::AID-MACP1745>3.0.CO;2-D)
34. Li S, Zou T (2011) Synthesis, Characterization of New Carboxylic Acid-Containing Benzoxazine and Its Cocuring Behaviors with Bisoxazoline. *J Appl Polym Sci*. <https://doi.org/10.1002/app.34535>
35. Tiptipakorn S, Punuch W, Okhawilai M, Rimdusit S (2015) Property enhancement of polybenzoxazine modified with monoanhydrides and dianhydrides. *J Polym Res* 22(7):132. <https://doi.org/10.1007/s10965-015-0771-x>