Synthesis and Characterization of a Hybrid Material Based on a Trimethoxysilane Functionalized Benzoxazine

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ABSTRACT: A polybenzoxazine/polysiloxane hybrid has been prepared by sol–gel process and ring-opening polymerization. For this purpose, first a functionalized benzoxazine was synthesized from bisphenol A, paraformaldehyde and 3-(trimethoxysilyl) propylamine, with initial molar ratio 1 : 4 : 2, and 95% yield. The structure of the monomer was characterized by Fourier transform infrared (FTIR) spectroscopy and nuclear magnetic resonance. The sol–gel process and curing behavior have been studied by FTIR spectroscopy and differential scanning calorimetry. The dynamic mechanical thermal analysis of the hybrid material (Bz-PSi) showed higher T_g and storage modulus respect to the conventional polybenzoxazine (Bz-BA). Also, the thermogravimetric analysis revealed a better thermal stability. The high limiting oxygen index (LOI) values (about LOI = 32) confirmed similar effective flame retardance properties of the hybrid material respect to conventional benzoxazine. © 2012 Wiley Periodicals, Inc. J Appl Polym Sci 000: 000–000, 2012

Key words: trimethoxysilane benzoxazine; hybrid polybenzoxazine; thermal properties

INTRODUCTION

Phenolic resins were the first synthesized resins and include synthetic thermosetting polymers obtained by the reaction between phenol and aldehydes.[1] They are widely produced industrially due to their flame and chemical resistances, electrical insulation, thermal stability, and low cost. However, phenolic resins have disadvantages both in processing and final properties, which limit their applications, such as corrosion in equipments due to the use of catalysts, presence of voids associated to the volatile byproducts and brittleness.[2]

As an alternative to traditional phenolic resins, a new type of versatile materials was developed: the polybenzoxazines.[3] They are obtained by thermally activated ring-opening of the 3,4-dihydro-2H-1,3-benzoxazines without any catalyst and without generating condensation byproducts.[4] These resins exhibit low volume contraction during the curing, low water absorption, improved electrical and mechanical properties, thermal and dimensional stability, and flame resistances.[5] Moreover, benzoxazine monomers can be simply prepared from phenols, primary amines, and formaldehyde, and their syntheses offer a wide range of molecular design flexibility to produce "tailor-made" polymers.[6]

Despite the improved properties that polybenzoxazines present, they exhibit low crosslink densities in comparison with the ordinary thermosetting resins, and their brittleness is similar to that of the traditional phenolic resins. To improve the properties, different strategies have been reported, such as the chemical modification of the structure by designing new monomers containing another reactive group such as phenylethynyl, allyl, propargyl, maleimide, by copolymerizing with other monomers as epoxy resins, or by blending with other polymers that exhibit improved thermal and mechanical properties.[7]

Polybenzoxazines with high flame retardant properties have attracted much attention owing to the development demands for electronic materials. According to the literature, the flame retardancy of polymers can be improved by incorporating bromine, phosphorus, or silicon units.[8] Brominated polybenzoxazines have been described,[9] as an alternative to brominated epoxy resins that have been used in particular in printed circuit boards due to their good flame retardant capacity and low cost.[10]

Phosphorus-containing groups can be introduced into polybenzoxazine via monomer modification. Recent development in flame retardant benzoxazines based on phenylphosphine oxide-containing biphenol have been reported.[11,12] Moreover, from the

cyclic organic phosphorus compound, 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO), and its derivatives have been synthesized by many flame retardant resins and among them a great number of DOPO-containing benzoxazines.[13–18] Other approaches for improving the flame retardancy of phosphorus-containing polybenzoxazines are the copolymerization of two or more benzoxazine monomers[13–16,19] or the copolymerization of benzoxazine with epoxy resins.[13,19,20] Also, phosphorus-containing benzoxazine-phenolic systems are reported.[21–23]

Recently, the incorporation of silicon to polybenzoxazine systems has been considered, but only in few cases, the flame retardant behavior was studied. The development of novel materials based on polybenzoxazines containing Si—O—Si linkages have been described using, in most cases, the sol–gel technology.[24–26] Ishida and Low[24] synthesized a hybrid benzoxazine from phenol, 3-(triethoxysilyl)propylamine and formaldehyde. The water molecules produced could be automatically separated from the product phase when a nonpolar solvent was used, as the benzoxazine portion of the product was insoluble in water, thus the triethoxyl groups of the silane were protected. However, Liu et al.[25] could not apply this method when they used 3-(trimethoxysilyl)propylamine probably due to the higher sensibility of trimethoxysilane units to hydrolysis. Therefore, they used a modified method, adding calcium hydride to the system, to remove the water molecules. In both cases, the hydrolysis and the condensation of the benzoxazine yielded organic–inorganic hybrids of polybenzoxazine with polysilsesquioxane exhibiting enhanced T_gs. Alternatively, the preparation of polybenzoxazine polydimethylsiloxane hybrids in situ by the ring opening polymerization of benzoxazine and the sol–gel process of diethoxydimethylsilane was described.[27,28] Moreover, the syntheses of benzoxazine-containing polyhedral oligomeric polysilsesquioxanes (POSS) and their polymerization were reported.[29,30] A silicon-containing benzoxazine monomer has been prepared from 1,3-bis(3-aminopropyl)-tetramethyldisiloxane, and it was demonstrated to be a high performance modifier for benzoxazine polymers.[31] Thermosetting polybenzoxazine resins from a benzoxazine having silicone units with UL-94 fire resistance rating V-0 have been patented.[32]

In a different approach, silicon-containing benzoxazine-epoxy copolymers have been obtained through the copolymerization of bisphenol A based benzoxazine and silicon-containing diglycidylderivative,[20] but nonflame retardant effect could be observed for the studied silicon percentages.

Other silicon-containing benzoxazine systems have been obtained by blending poly(dimethylsilyleneethynylenephenyleneethynylene) (DMSEPE) and an acetylene functionalized benzoxazine (AFBEN),[33] from oligosiloxane- or polysiloxane-containing thermally curable benzoxazine units in the main chain,[34,35] or from main chain polybenzoxazine-block-polydimethylsiloxane multiblock copolymers.[36]

In this work, a novel type of benzoxazine/trimethoxysilane hybrid was synthesized from bisphenol A, paraformaldehyde, and 3-(trimethoxysilyl) propylamine. The polybenzoxazine/polysiloxane thermosetting was prepared by sol–gel process and ring-opening polymerization. The processes were studied by Fourier transform infrared (FTIR) spectroscopy and differential scanning calorimetry (DSC) and thermal, dynamic mechanical, and flame retardant properties were evaluated.

EXPERIMENTAL

Materials

The following chemicals were obtained from the sources indicated: bisphenol A (97%), 3-(trimethoxysilyl) propylamine (95%), and calcium hydride from Aldrich (USA), aniline from Merck (Germany), paraformaldehyde and hydrochloric acid (ca. 36% HCl) from Cicarelli (Argentina). Bisphenol A based benzoxazine (Bz-BA) was prepared as previously described.[37] All solvents were used as received without purification.

Synthesis of trimethoxysilane based benzoxazine (Bz-Si)

Into a three-neck round-bottom flask equipped with a magnetic stirrer, a dropping funnel, and a reflux condenser, chloroform (150 mL), paraformaldehyde (4,8 g, 0.17 mol), and calcium hydride (4 g) were added, and the mixture was heated at 60°C under nitrogen. Then, 3-(trimethoxysilyl) propylamine (15 g, 0.08 mol) was added dropwise, the temperature was raised to 75°C, and then the bisphenol A was slowly added (10 g, 0.04 mol). Finally, the temperature was increased at 80°C. The reaction was followed by thin layer chromatography using hexane : ethyl acetate (1 : 1) as solvent system. The total reaction time was 3 h. The solid residues were filtered out, and the solvent was evaporated at reduced pressure to give a clear oil (95% yield). In the reaction medium, the calcium hydride was incorporated to remove the water molecules, by precipitation of the calcium hydroxide formed.

^{1}H-NMR (CDCl3/TMS, δ (ppm)): 6.90 (2H, d), 6.83 (2H, d); 7.12 (2H), 6.65 (2H); 4.80 (4H, s); 3,99 (4H, s), 3.68 (18H, s), 2.78 (4H, m), 1.70 (4H, m), 1.60 (6H, s), 0.68 (4H, m).

^{13}C-NMR (CDCl3, δ (ppm)): 144.01 (s), 135.00 (s), 119.99 (s); 114.70 (s); 110.05 (s), 79.88 (s), 54.85 (s), 50.15 (s), 50.11 (d), 43.63 (s), 32.52 (d) 22.07 (s), 10.01 (s).

FTIR: 930 cm^{-1} (oxazine ring st), 1035 cm^{-1} (Ar-O—C st), 1077 cm^{-1} (Si—O—Me st), 1228 cm^{-1} (C—O—C st), 1494 cm^{-1} (C—C Ar st).

Preparation of the precursor hybrid (Bz-PSi)

Bz-Si monomer (2 g) and isopropanol (5 mL) were added to a flask provided with magnetic stirred at room temperature. Then, 2 mL of aqueous HCl solution (0.0001 mol) was added, and the hydrolysis and condensation were performed for 12 h at room temperature. The solvent was evaporated at 60°C in vacuum for 4 h.

Crosslinking reactions

To study the curing reaction of Bz-BA and Bz-PSi, the polymerization was monitored by dynamic DSC using a heating rate of 10°C min^{-1} with a temperature range of 30–350°C.

Molded cured benzoxazines were prepared with a manual hydraulic press 15-ton sample equipped with a water cooled heated platens. The samples were placed in 70 × 50 × 1.9 mm^3 or 70 × 6 × 3 mm^3 molds and compression molded under 0.1 mPa. The curing of the hybrid benzoxazine involved curing cycles of 100°C for 1 h, 180°C for 2 h, 220°C for 2 h, and 225°C for 2 h. The curing of Bz-BA was performed at 180°C for 2 h, 200 for 1 h, and 220°C for 2 h.

Characterization

^{1}H 400 MHz and ^{13}C 100.5 MHz nuclear magnetic resonance (NMR) spectra were obtained using a Varian Gemini 400 spectrometer with Fourier transform, CDCl$_3$ as solvent and TMS as internal standard.

The FTIR spectra were recorded on a JASCO 680 FTIR spectrophotometer with a resolution of 4 cm^{-1} in the absorbance mode and equipped with an attenuated total reflection (ATR) accessory with thermal control and a diamond crystal (Golden Gate heated single-reflection diamond ATR, Specac. Teknokroma).

Calorimetric studies were performed on a Mettler DSC821e thermal analyzer using N$_2$ as a purge gas (20 mL min^{-1}) at scanning rate of 10°C min^{-1}. Thermal stability studies were performed in a Mettler TGA/SDTA851e/LF/1100 with N$_2$ and air as gases (100 mL min^{-1}) at scanning rates of 10°C min^{-1}.

Morphologies of the sample surfaces were evaluated by Scanning Electron Microscope (SEM) with digital imaging system; JEOL, model JSM-35C, at an activation voltage of 20 kV.

Mechanical properties were measured using a dynamic mechanical thermal analysis apparatus (TA DMA 2928). Specimens (70 × 6 × 1.9 mm) were tested in a single cantilever configuration. The thermal transitions were studied in the range of 30–250°C at a heating rate of 5°C min^{-1} and at a fixed frequency of 1 Hz.
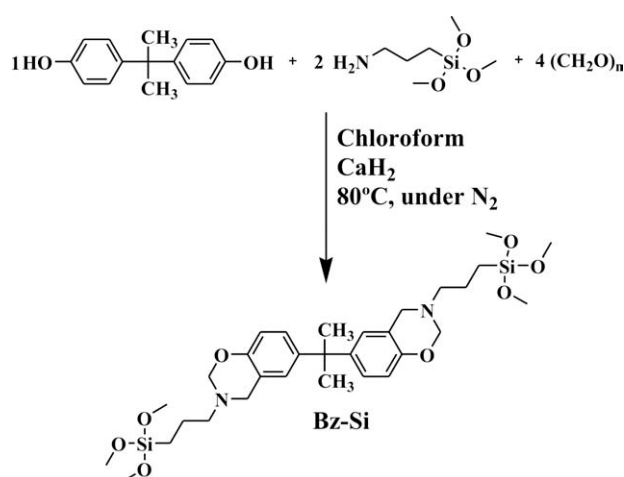
Scheme 1 Synthesis of benzoxazine containing trimethoxysilane (Bz-Si).

Regarding the flame retardant properties, limiting oxygen index (LOI) measurements (LOI-ASTM-2863) and UL-94-modified flammability test were performed. LOI measurements were performed on a Stanton Redcroft FTA flammability unit provided with an Oxygen Analyzer. UL-94-modified flammability test (from the Underwriters Laboratories) was similar to standard American Society for Testing and Materials (ASTM) method and National Fire Protection Association (NFPA) (Underwriters Laboratories, 1991) method.[38] Samples of 70 × 6 × 3 mm^3 were prepared by molding.

RESULTS AND DISCUSSION

Several works that investigate the development of novel materials based on polybenzoxazines containing Si—O—Si linkages have been described using, in most cases, the sol–gel technology as an effective and inexpensive method.[24–28] The sol–gel process involves two different stages: hydrolysis and polycondensation reactions of the alcoxy groups that lead to the formation Si—O—Si network.

Scheme 1 describes the general synthesis of new Bz-Si that was prepared from bisphenol A, paraformaldehyde, and 3-(trimethoxysilyl) propylamine, with initial molar ratio 1 : 4 : 2, involving a Mannich-type reaction.[3] Using the procedure described above, the Bz-Si with a yield of 95% was obtained.

The structure of Bz-Si and its purity were verified by FTIR and NMR spectroscopies. In Figure 1, the IR spectrum of the Bz-Si is shown. It can be observed that the characteristic absorptions at 930 cm^{-1}, 1228 cm^{-1}, and 1494 cm^{-1} corresponding to the oxazine ring, as well as the absorption at 1077 cm^{-1} corresponding to the Si—O—Me bonds. The absence of vibrations in the range of 3500–3100 cm^{-1},
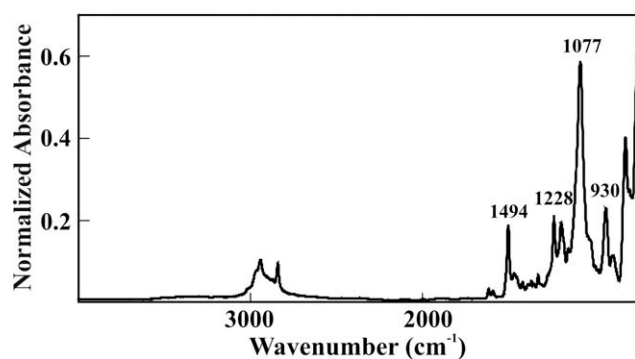
Figure 1 FTIR spectrum of Bz-Si monomer.

characteristic of hydroxyl groups indicates that no dimers or oligomers were formed.

The ^{1}H- and ^{13}C-NMR spectra of Bz-Si and the assignment of the signals are shown in Figure 2. In ^{1}H-NMR spectrum, the signal at 3.7 ppm (18 H) corresponds to Si—O—CH_3. The signals at 4.0 ppm (4H) and 4.8 ppm (4H) were assigned to the O—CH_2—N and Ph—CH_2—N of the oxazine ring, respectively, that indicates the formation of benzoxazine ring. No signal corresponding to N—CH_2—Ph at 3.8 ppm resulting from the ring opening of benzoxazine was detected, indicating the high purity of synthesized benzoxazines. The aromatic signals appear between 6.5 and 7.0 ppm (8H). Figure 2 shows the ^{13}C-NMR spectrum with characteristic signals at 50.43 and 80.10 ppm of the methylene carbons in the oxazine ring.

The hybrid precursor Bz-PSi was prepared by hydrolysis and condensation of hexafunctional Bz-Si catalyzed by hydrochloric acid to afford a benzoxazine containing oligomeric polysilsesquioxane (Scheme 2).

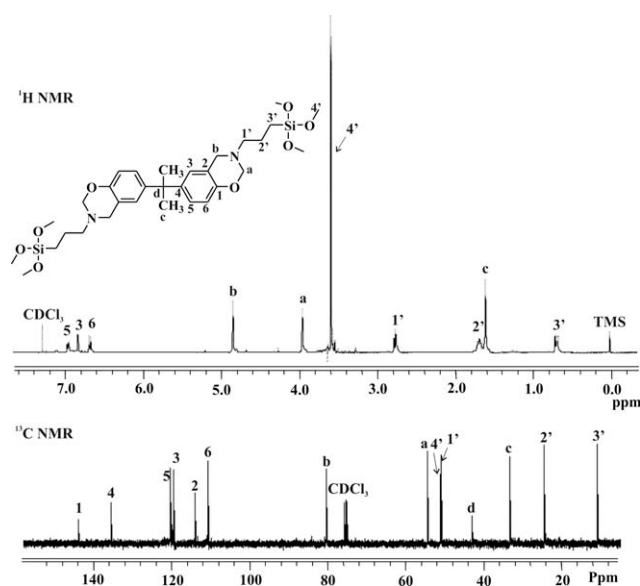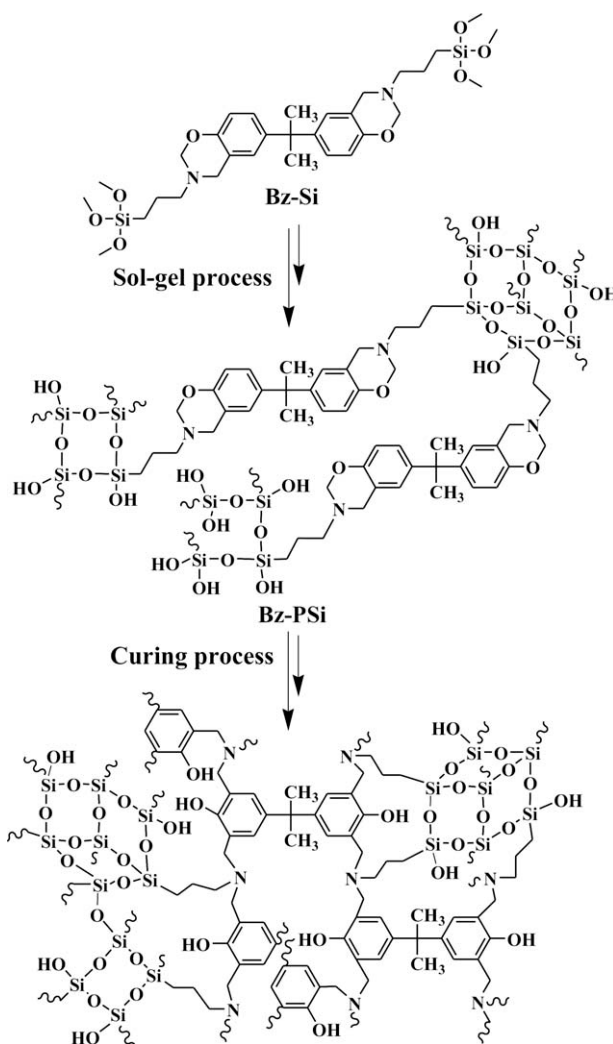Curing reaction of Bz-PSi was studied by DSC and FTIR spectroscopy. Bz-BA was also included for

Scheme 2 Sol–gel process of Bz-Si (partially condensed) and curing process of the hybrid Bz-PSi.

comparison purposes. Figure 3 shows the DSC thermograms. The crosslinking exotherm of Bz-BA indicates that the ring opening reaction of the oxazine starts about 210°C, and a typical polymerization exotherm for difunctional benzoxazines centered at 245°C is observed (see Table I). As it is well known, the Bz-BA exhibits one dominant autocatalytic curing process that generates a phenolic Mannich bridge network. On the other hand, the thermal treatment of Bz-PSi involved two scans [Fig. 3(b,c)]. The first (3b) was made from 30°C to 180°C at 10°C min^{-1}, and the second (3c) from 30°C to 350°C at 10°C min^{-1}. It can be observed that a first exotherm at low temperatures (about 90°C) due to the incomplete sol–gel process, and the ring opening reaction of the oxazine with a maximum centered at 265°C. No catalytic effect of the silanol groups formed in the sol–gel process is observed, and a rigid structure of polysiloxane was formed.

Figure 4 shows FTIR spectra along the Bz-PSi and Bz-BA polymerizations. The curing of the Bz-PSi involved cycles of 100°C for 1 h, 180°C for 2 h,
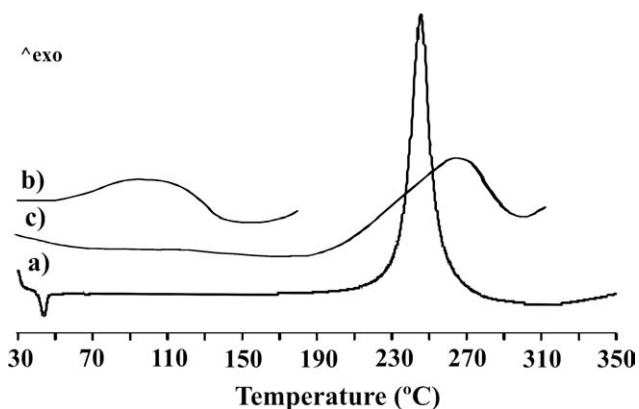

Figure 2 ^{1}H- and ^{13}C-NMR spectra of Bz-Si.

Figure 3 DSC thermograms of (a) Bz-BA, (b) Bz-PSi first scan from 30°C to 180°C [first scan], and (c) Bz-PSi after thermal treatment [second scan].

TABLE I
Characteristics of the Benzoxazines Crosslinking

Samples	%Si	%N	T_{onset}[a]	T_{max}[b]	$\Delta H°$ (kJ mol^{-1})[c]	T_g (°C) Tan δ_{max}	E''
Bz-BA	–	6.23	210	245	146	172	154
Bz-PSi	8.65	4.45	190	270	100	235	210

[a] Initial temperature of the crosslinking exotherm.
[b] Temperature of the maximum heat release rate.
[c] Reaction enthalpy values extrapolated to zero heating rate.

220°C for 2 h, and 225°C for 2 h, and the curing of Bz-BA cycles of 180°C for 2 h, 200°C for 1 h, and 220°C for 2 h. FTIR technique allows following the evolution of the functional groups involved in the processes by means of the absorption variations. From Bz-BA spectra of Figure 4(A), it can be observed the progressive diminution with time of the characteristic benzoxazine bands at 1485 cm^{-1}, 1222 cm^{-1}, and 943 cm^{-1}, indicating the homopolymerization.

From b and c spectra of Figure 4(B), a progressive increase of the bands at 888 cm^{-1} and 1030 cm^{-1} corresponding to silanol groups (Si—OH) and siloxanes (Si—O—Si), respectively, is detected due to the sol–gel process. In d, e, and f spectra, a decrease of the bands at 930 cm^{-1}, 1228 cm^{-1}, and 1494 cm^{-1} is observed, indicating the ring opening of the oxazine during the curing. Furthermore, in the same spectra a progressive diminution of the Si—OH band at 888 cm^{-1}, and an increment of the Si—O—Si band at 1036 cm^{-1} can be seen, indicating that the polysiloxane matrix formation, by polycondensation of the silanol groups during the curing, also occurs. In Figure 5, the morphologies of the films obtained by SEM are shown, revealing homogeneous films without phase separation. The IR results of the Bz-PSi suggest synchronized reactions corresponding to the
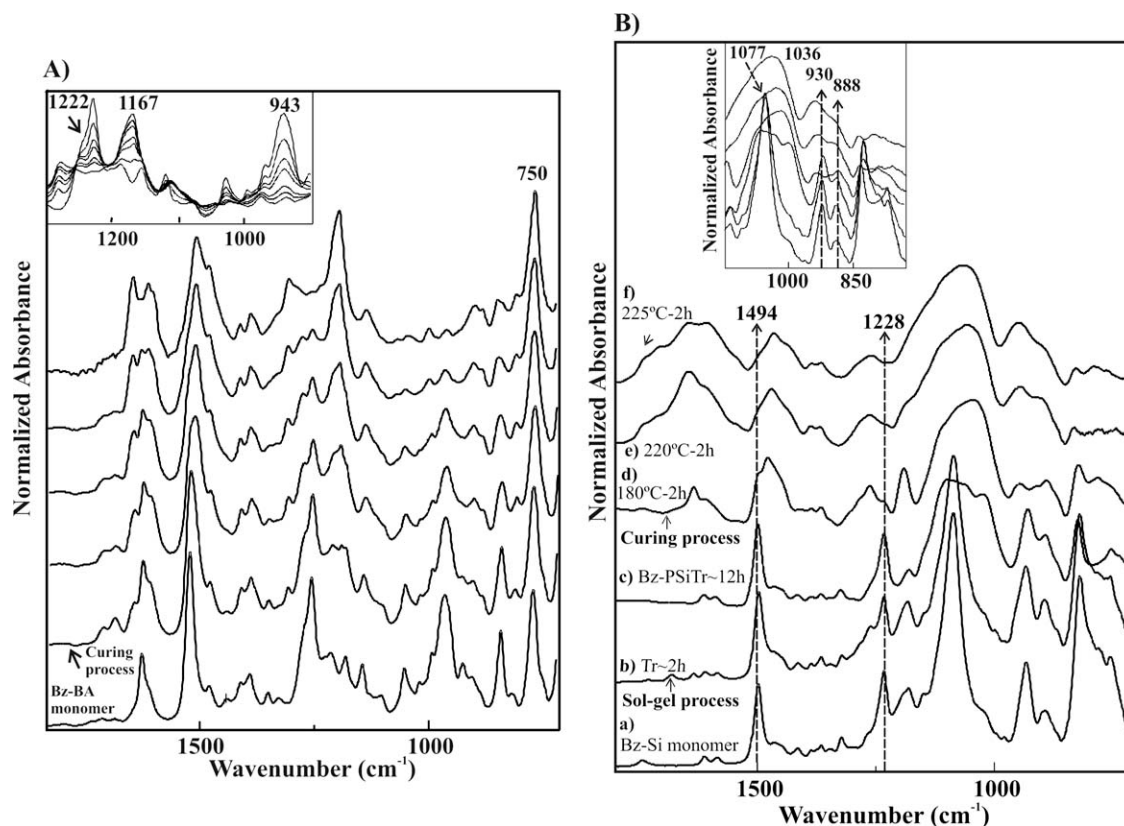

Figure 4 IR spectra of: (A) Bz-BA curing process, and (B) Bz-PSi sol–gel and curing processes.
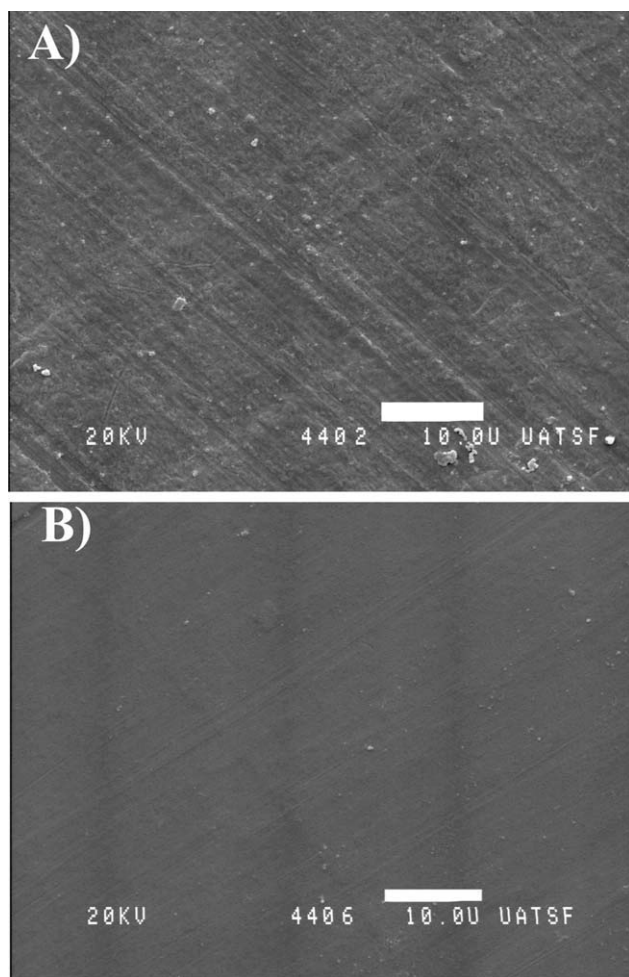
Figure 5 SEM micrographs (10 μm) of (a) Bz-BA and (b) Bz-PSi.

Figure 6 Storage modulus and loss factor of Bz-BA and Bz-PSi.

sol–gel process and ring opening that allow explaining the homogeneous hybrid film obtained.

The dynamic mechanical and thermogravimetric properties of the polybenzoxazines were investigated. The networks were prepared by heating samples according to DSC and FTIR data. The curing of the Bz-PSi involved cycles of 100°C for 1 h, 180°C for 2 h, 220°C for 2 h, and 225°C for 2 h. Also, a curing of Bz-BA was performed to compare at 180°C for 2 h, 200°C for 1 h, and 220°C for 2 h.

The dynamic mechanical behavior of the cured benzoxazine resins was obtained as a function of the temperature (Fig. 6). The crosslinking density of a polymer can be estimated from the plateau of the elastic modulus in the rubbery state.[39] However, this theory is strictly valid only for lightly crosslinked materials and was therefore used only to make qualitative comparisons of the level of crosslinking among several polymers. As it can be seen, the crosslinking density of Bz-PSi is higher than that of the crosslinking density of Bz-BA. Figure 6 shows the plots of loss factor (Tan δ) versus temperature.
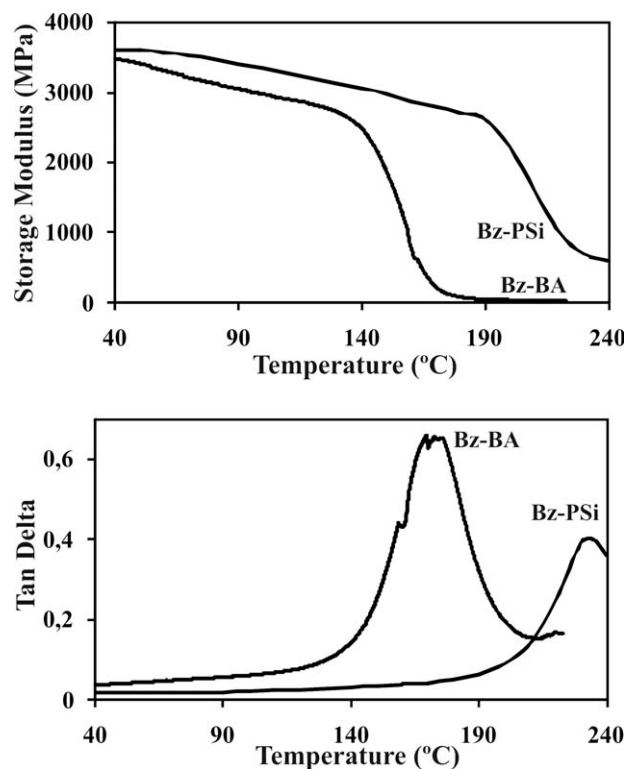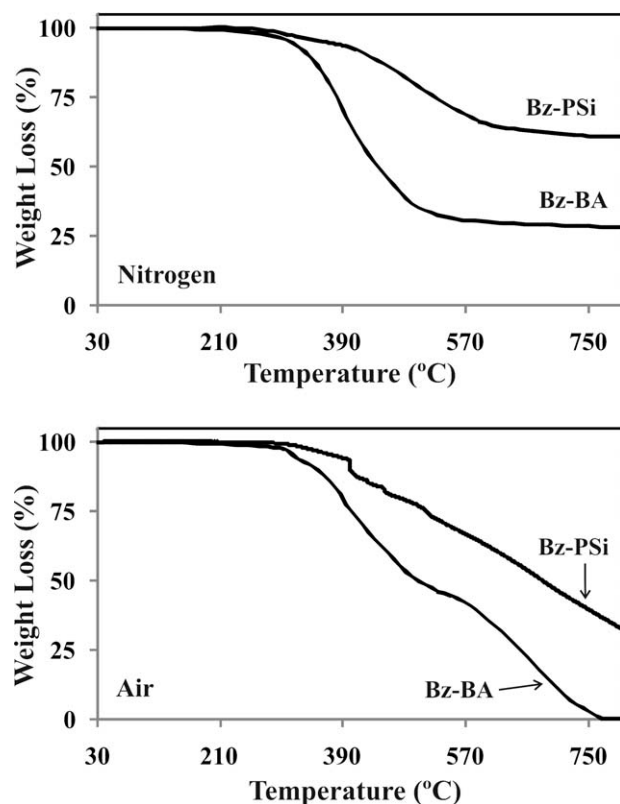

Figure 7 TGA plots in nitrogen and air of Bz-BA and Bz-PSi.

TABLE II
Thermogravimetric and Flame Retardant Properties of Polybenzoxazines

Samples	Nitrogen			Air			UL-94	LOI (% O_2 v/v)
	$T_{5\%}$[a] (°C)	T_{max}[b] (°C)	$CY_{800°C}$[c] (%)	$T_{5\%}$[a] (°C)	T_{max}[b] (°C)	$CY_{800°C}$[c] (%)		
Bz-BA	313	391	30	322	396, 740	0	V-0	31.8
Bz-PSi	450	570	60	400	–	34	V-0	32.0

[a] Temperature of 5% weight loss.
[b] Temperature of the maximum weight loss rate.
[c] Char yield at 800°C.

The T_gs of the crosslinked materials can be estimated from the maximum of the loss modulus (E'') or from the α relaxation peak of the loss factor. Table I shows the T_g values obtained from both measurements. The results indicate that the T_g of the hybrid material Bz-PSi is higher than that of the Bz-BA. This can be explained by the lower segmental mobility associated to the presence of the inorganic polysiloxane matrix.

The thermal stability and the degradation behavior of the materials were investigated by thermogravimetric analysis (TGA) under nitrogen and air atmospheres. In Figure 7, the weight loss as a function of temperature is shown for both systems (Bz-PSi and Bz-BA), and Table II summarizes the thermogravimetric results. The thermograms of Figure 7 indicate that stability and decomposition behaviors are improved by the addition of siloxane. The siloxane content allows the formation of a highly stable network due to the better stability of Si—O bond in comparison with C—C and C—O bonds. As it is shown in Table II, the char yield under nitrogen atmosphere is 60% for Bz-PSi and 30% for Bz-BA, and weight loss rate of Bz-PSi is significantly lower than that of the Bz-BA. Under air atmosphere, the char yield is 34% for Bz-PSi and 0% for Bz-BA due to the thermoxidative degradation. The behavior of Bz-PSi is associated to the formation of stable silica, which tends to migrate to the char surface serving as a protection layer to prevent further degradation of char at high temperatures.[20] Also, the thermal stability of the hybrid was enhanced with respect to other similar structures synthesized.[25]

The flame retardancy of the materials was evaluated from LOI and UL-94 tests. The results are presented in Table II. The LOI values indicate that both materials are excellent flame retardant. However, no significant differences in LOI values between both polybenzoxazine systems were observed. UL-94 tests revealed V-0 degree, validating the good flame retardancy of both materials observed from LOI measurements.

CONCLUSIONS

A hybrid benzoxazine was synthesized from bisphenol A, paraformaldehyde, and 3-(trimethoxysilyl)-propylamine, with initial molar ratio 1 : 4 : 2, and a 95% yield. The sol–gel process and ring opening reactions during the curing were detected by DSC and IR spectroscopy, indicating synchronized processes at the curing temperatures that allow obtaining a homogeneous hybrid film. The presence of the inorganic structure of polysiloxane improves the thermal and dynamic-mechanical properties of the polybenzoxazine. The hybrid material exhibited increases in T_g and storage modulus due to the restricted segmental mobility of the chains by the presence of the inorganic matrix.

The hybrid material showed higher thermal stability and char than the Bz-BA. Finally, the values of LOI and the results of UL-94 test, showed their excellent flame retardant properties.

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