COPOLYMERIZATION OF A SILICON-CONTAINING SPIROORTHOESTER WITH A PHOSPHORUS-CONTAINING DIGLYCIDYL COMPOUND. INFLUENCE IN FLAME RETARDANCE AND SHRINKAGE

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Abstract

The cationic copolymerization of spiroorthoesters with diglycidyl compounds to introduce silicon and phosphorus has been carried out with ytterbium triflate as an initiator. The curing process was studied by Differential Scanning Calorimetry and monitored by Fourier Transform Infrared Spectroscopy. The thermomechanical and thermogravimetric properties were evaluated. The incorporation of phosphorus or silicon into the network increased the limiting oxygen index values, thus improving the flame retardance of the materials. The shrinkage during crosslinking for all mixtures was lower than that observed in conventional epoxy resins.

Keywords: cationic polymerization; heteroatom-containing polymer; flame retardance; crosslinking; spiroorthoester

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INTRODUCTION

In recent modern industry, epoxy resins play an important role due to their excellent characteristics of great versatility, toughness, good moisture resistance, solvent and chemical resistance, outstanding adhesion, and superior electrical an mechanical properties. So, they are

widely applied in surface coating, adhesives, painting, composites, laminates, en-capsulants for semiconductor and insulating materials for electrical devices, etc.[1,2] However, epoxy resins have two main disadvantages: one is their flammability and the other is the shrinkage on curing. Up to now, research efforts on improving the properties of epoxy resins are under progress for meeting the require-ments from the versatile and advanced applications. For epoxy resins used in electronics, superior thermal stability, electrical properties, and halogen-free in flame retardation were specially focused. The halogen-free flame retardants are environ-mentally friendly because they generate less toxic and corrosive substances during fire. The common halogen-free flame retardants are mainly organophosphorus[3,4] and organosilicon[5,6] compounds. Both elements are described that can function in the condensed phase or vapor phase, and possibly con-currently in both phases.[7]

Phosphorus-containing polymers confer fire resistance mainly by modifying the thermal decom-position of the polymers, in favor of reactions yielding carbonaceous char rather than CO and CO_2. They form a surface layer of protective char during fire before the unburned material begins to decompose. The char layer acts as a barrier to inhibit gaseous products from diffusing to the flame and to shield the polymer surface from heat and air.[4,8,9] However, oxidation of phosphorus char is observed at temperatures higher than 600 ºC.[10,11] The efficiency of flame retardation of phosphorus basically depends on the amount of char formation; thus, by improving the thermal stability of phosphorus char at high temperatures could be improved the flame-retardancy efficiency. Silicon-containing poly-mers are described that can degrade forming thermally stable silica, which have the tendency to migrate to the char surface serving as a protection layer to prevent further degradation of char at high temperatures.[5,12]

Although, phosphorus or silicon compounds could be used alone as flame retardants, recently, when the flame retardants simultaneously contained both elements some synergistic effect has been described.[12-14] The reason for this synergistic effect is that phosphorus offers the tendency of char formation and silicon provides the thermal stability of the forming char during fire.[6,14-16]

Another problem of the epoxy resins is their shrinkage during curing, because the monomer molecules are located at a van der Waals distance from one another, while in the corresponding polymer the mono-meric units move to a covalent distance of each other. Thus, the atoms are much closer to one another in the polymer than

they were in the original monomer. This shrinkage can lead to internal compressive stress in the material, poor adhesion of coatings to the substrate, and the appearance of microvoids and microcracks, which reduce the durability of materials.[17] One of the best solutions to solve the shrinkage is the use of monomers that show no volume shrinkage in their polymerization, such as spiroorthoesters (SOEs),[18,19] spiroor-thocarbonates (SOCs)[20,21] and bicy-clicorthoesters (BOEs).[22]

The aim of the present study is to reduce together the above mentioned disadvantages of epoxy resins by means of the cationic crosslinking of a new silicon-containing spiro-orthoester with mixtures of DGEBA and a phosphorus-containing glycidyl derivative. Also, the aim of this study is to investigate the possible synergistic effect of phosphorus-silicon on flame retardancy.

The cationic crosslinking was carried out with ytterbium triflate as initiator, which has shown to be effective to polymerize glycidyl compounds and spiroorthoesters.[23] This crosslinking was studied with differential scanning calorimetry (DSC) and Fourier transform infrared spectroscopy (FTIR). The materials were charac-terized by DSC, thermogravimetric analysis (TGA), and thermodyna-momechanical analysis (DMTA). The volume change was evaluated with a Micromeritics gas pycnometry and the flame retardancy was tested by the limiting oxygen index (LOI) measurements.

EXPERIMENTAL

Materials

Glycidol (Aldrich), glycidyl isopropyl ether (Aldrich), γ-butirolactone (γ-BL; Aldrich), boron trifluoride diethyl etherate ($BF_3.OEt_2$; Aldrich), triethyl-amine (Fluka), trimethylsilylpropionic acid (Fluorochem), N-(3-Dimethyl-amino-propyl)-N'-ethyl-carbodiimide hydrochloride (EDC; Fluka), 4-(dimethylamino)pyridine (DMAP; Fluka), 1,4-benzoquinone (Aldrich), epichlorohydrin (EPC; Fluka), benzyl-trimethylammonium chloride (BTMA; Fluka), DGEBA (Epikote Resin 827, Shell Chemicals; epoxy equivalent = 182.08), ytterbium(III) trifluorome-thanesulfonate [Yb(OTf)$_3$; Aldrich] were used as received. Commercial DOPO was kindly supplied by Aismalibar and it was purified before use by heating at 130 ºC under vacuum for 2 h and then gradually heated to 150 ºC. The purified product was cooled to room temperature under argon atmosphere. All solvents were purified by standard procedures.

Instrumentation

NMR spectra (^{1}H, 400 MHz; ^{13}C 100.6 MHz) were obtained with a Varian Gemini 400 spectrometer

with Fourier transform, and $CDCl_3$ as the solvent.

Crosslinking studies were performed on a Mettler DSC-821e thermal analyzer in covered Al pans under nitrogen at scan rates of 10 ºC/min. The determination of glass transition temperatures (T_g's) were carried out on a Mettler DSC-822e thermal analyzer in covered Al pans under N_2 at scan rates of 20 ºC/min. The samples weighed approximately 8 mg.

The IR spectrums were recorder with a 680 Plus FTIR spectrophotometer with a resolution of 4 cm^{-1} in the absorbance mode.
TGAs were carried out with a Mettler TGA/SDTA 851e thermobalance. Cured samples with an approximate mass of 10 mg were degraded between 30 ºC and 800 ºC at a heating rate of 10 ºC/min in atmosphere of N_2 or air.

Thermodinamomechanical analysis (DMTA) were carried out with a TA DMA 2928 thermal analyzer, working with three point bending clamp from -50 ºC to 200 ºC with a heating rate of 5 ºC/min and at fixed frequency of 1 Hz.

The densities of the materials were measured with a Micromeritics Accu-pyc 1330 TC gas pycnometer at 30 ºC.

Limiting oxygen indices were measured on a Fire Testing Techno-logy flammability unit in conformance with ASTM D 2863 for samples measuring 100 mm x 6 mm x 3 mm.

Synthesis of *2-hydroxymethyl-1,4,6-trioxaspiro [4,4] nonane (SOE-OH)*

Glycidol (30 g, 0.40 mol) was added dropwise over a period of 15 min at a temperature below 10 ºC in an argon atmosphere to a mixture of 200 g (2.3 mol) of γ-BL and 1.0 mL (7.9 mmol) of $BF_3.OEt_2$ as a catalyst. After the addition was completed, the mixture was stirred for 60 min at the same temperature. The reaction was quenched by the addition of 1.4 mL (10 mmol) of triethylamine. After the solvent was removed under reduced pressure, the residue was distilled fractionally to yield 11.2 g (17%) of a transparent, colorless liquid.

^{1}H NMR ($CDCl_3$, two diastereomers): δ(ppm) = 4.41-4.32 (m, 2H, -O-CH-), 4.14-4.03 (m, 2H, -O-CH_2-), 3.99-3.89 (m, 4H, -O-CH_2-), 3.85-3.80 (m, 2H, -O-CH_2-), 3.73-3.54 (m, 4H, -CH_2-OH), 2.89 (br, 2H, OH), 2.18-2.12 (m, 4H, -CH_2-), 2.05-1.97 (m, 4H, -CH_2-).

^{13}C NMR ($CDCl_3$, two diastereomers): δ(ppm) = 129.60 (s, spiranic C), 129.32 (s, spiranic C), 75.99 (s, -O-CH-), 67.42 (s, -O-CH_2-), 65.69 (s, HO-CH_2-), 64.92 (s, OH-CH_2-), 62.81 (s, -O-CH_2-), 62.54 (s, -O-CH_2-), 32.67 (s, -CH_2-), 32.50 (s, -CH_2-), 24.51 (s, -CH_2-), 24.35 (s, -CH_2-).

Synthesis of 1,4,6-trioxaspiro[4,4]-2-nonylmethyl 3-trimethylsilyl propio-nate (SOE-Si)

Under an argon atmosphere, an oven-dried 100 mL round-bottom flask containing 20 mL of anhydrous dichloromethane was charged with 1.0 g (6.8 mmol) of trimethylsilyl propionic acid, 1.09 g (6.8 mmol) of SOE-OH, 1.44 g (7.5 mmol) of EDC, and 0.91 g (7.5 mmol) of DMAP. The solution was stirred and heated at 40 ºC for 3 h. After cooling to room temperature, the solution was washed with two 30-mL portions of a 10% citric acid solution, twice with 30-mL portions of 10% sodium bicarbonate solution, and twice with brine. The organic solution was dried over anhydrous magnesium sulfate, and the solvent was removed by evaporation to give 1.97 g (90%) of a transparent, colorless liquid.

^{1}H NMR (CDCl$_3$, two diastereomers): δ(ppm) = 4.37-4.34 (m, 1H, -O-CH-), 4.24-4.21 (m, 1H, -O-CH-), 4.15-4.13 (m, 2H, -O-CH$_2$-), 4.12-3.96 (m, 4H, -CH$_2$-OCO-), 3.86-3.75 (m, 4H, -O-CH$_2$-), 3.69-3.64 (m, 2H, -O-CH$_2$-), 3.63-2.14 (m, 4H, -CH$_2$-COO-), 2.08-1.99 (m, 4H, -CH$_2$-), 1.91-1.85 (m, 4H, -CH$_2$-), 1.19-0.69 (m, 4H, -Si-CH$_2$-), -0.08 (s, 8H, -CH$_3$).

^{13}C NMR (CDCl$_3$, two diastereomers): δ(ppm) = 174.63 (s, -COO-), 129.69 (s, spiranic C), 129.61 (s, spiranic C), 74.20 (s, -O-CH-), 73.32 (s, -O-CH-), 67.21 (s, -O-CH$_2$-), 67.14 (s, -O-CH$_2$-), 65.99 (s, -O-CH$_2$-), 65.89 (s, -CH$_2$-OCO-), 64.95 (s, -CH$_2$-O-), 64.05 (s, -O-CH$_2$-), 32.61 (s, -CH$_2$-), 28.56 (s, -CH$_2$-COO-), 24.17 (s, -CH$_2$-), 23.98 (s, -CH$_2$-), 11.47 (s, -Si-CH$_2$-), -2.03 (s, -CH$_3$).

Synthesis of 2-(isopropoxymethyl)-1,4,6-trioxaspiro [4,4]-2-nonane (SOE-iso)

Glycidyl isopropyl ether (25 g, 0.2 mol) was added dropwise over a period of 20 min at a temperature below 10 ºC in an argon atmosphere to a mixture of 55 g (0.6 mol) of γ-BL and 0.52 mL (4.1 mmol) of BF$_3$.OEt$_2$ as a catalyst. After the addition was completed, the mixture was stirred for 2 h at the same temperature. The reaction was quenched by the addition of 1.0 mL (7.2 mmol) of triethylamine. After the solvent was removed under reduced pressure, the residue was distilled fractionally to yield 12.1 g (28 %) of a transparent, colorless liquid.

^{1}H NMR (CDCl$_3$, two diastereomers): δ(ppm) = 4.38-4.31 (m, 1H, -O-CH-), 4.24-4.20 (m, 1H, -O-CH-), 4.12-4.07 (m, 2H, -O-CH$_2$-), 3.91-3.87 (m, 2H, -O-CH$_2$-), 3.78-3.76 (m, 4H, -O-CH$_2$-), 3,66-3.32 (br, 6H, -O-CH$_2$-, -CH$_3$-<u>CH</u>-), 2.12-2.10 (m, 4H, -CH$_2$-), 2.01-1.94 (m, 4H, -CH$_2$-), 1.12 (s, 12H, -CH$_3$).

^{13}C NMR (CDCl$_3$, two diastereomers): δ(ppm) = 129.60 (s,

spiranic C), 75.58 (s, -O-CH-), 74.69 (s, -O-CH-), 72.44 (s, -CH$_3$-C$\underline{H}$-), 69.82 (s, -O-CH$_2$-), 68.58 (s, -O-CH$_2$-), 67.51 (s, -O-CH$_2$-), 67.34 (s, -O-CH$_2$-), 67.86 (s, -O-CH$_2$-), 33.00 (s, -CH$_2$-), 32.89 (s, -CH$_2$-), 24.39 (s, -CH$_2$-), 24.28 (s, -CH$_2$-), 22.01 (s, CH$_3$).

Synthesis of 10-(2',5'-bis(glycidyl-oxy)phenyl)-9, 10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO-BQ-Gly)

DOPO-BQ-Gly was synthesized from DOPO and benzoquinone in a first step reaction, and this was followed by the reaction of the two phenolic groups with EPC and BTMA as a catalyst, as is described in the literature.[24,26]

Crosslinking reactions

The cationic crosslinking reactions were carried out by mixing the corresponding monomers in a molar ratio diglycidyl/SOE 2:1 with 1 phr of ytterbium triflate (1 phr = 1 part per 100 parts of the monomer mixture weight/weight). The composition of the mixtures is listed in Table 1. The sample bars used for dynamo-mechanical and thermogravimetric analysis and burn tests were cured in aluminium molds by heating in an

oven. The curing conditions were established by Dynamic Differential Scanning Calorimetry and are also listed in Table 1.

RESULTS AND DISCUSSION

First, we synthesized the starting spiroorthoesters: SOE-Si and SOE-iso, one of them containing silicon in its structure, and the phosphorus-containing glycidyl compound (DOPO-BQ-Gly) (Scheme 1). SOE-Si was synthesized as previously described[26] by an esterification reaction between a commercially trimethylsilylpropionic acid and a previously synthesized hydroxyl-containing spiroorthoester (SOE-OH) under mild conditions using EDC and DMAP. The intermediate SOE-OH and the SOE-iso monomers were synthesized by a cyclization reaction between γ-BL and a glycidyl compound: glycidol or glycidyl iso-propyl ether respectively. The phosphorus-containing glycidyl mo-nomer (DOPO-BQ-Gly) was synthe-sized by a two steps reaction. First, DOPO was reacted with benzo-quinone,[24] followed by the reaction of the two phenolic groups with EPC in excess and BTMA as a catalyst.[25]

Silicon and phosphorus were introduced into the network from a silicon-containing spiroorthoester and a phosphorus-containing diglycidyl compound. To introduce different phosphorus and silicon contents in the mixtures, commercial DGEBA and an aliphatic spiroorthoester, SOE-iso, were also used. In all cases, the ratio of diglycidyl compounds:SOEs was 2/1 (mol/mol).
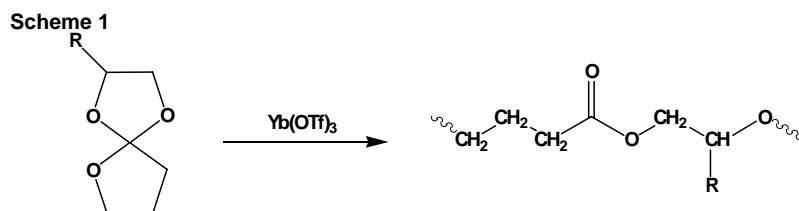

Scheme 1

Polym Degrad Stab (submitted)
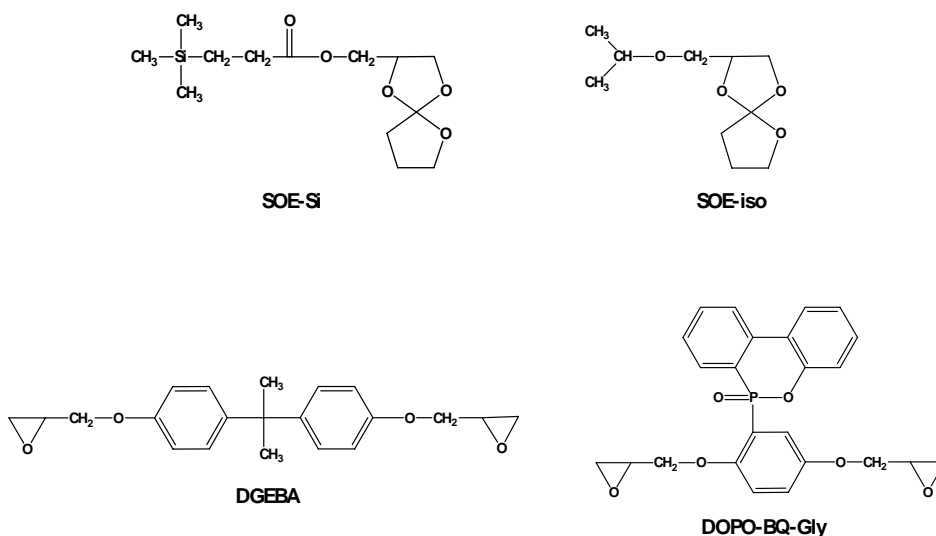
In the cationic copolymerization of epoxy resins with spiroorthoesters three different processes are expec-

a) Copolymerization of glycidyl compounds with SOE
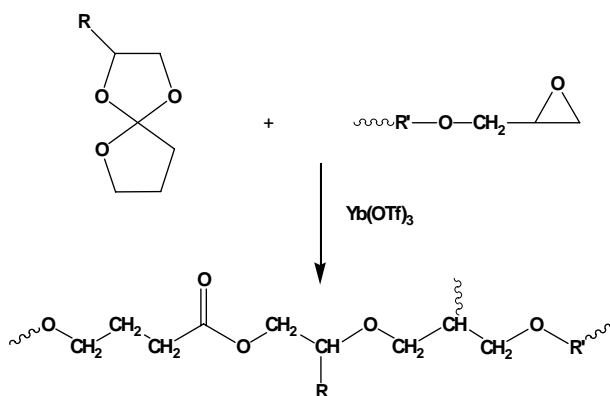
Scheme 1

b) Homopolymerization of SOEs

c) Homopolymerization of glycidyl units
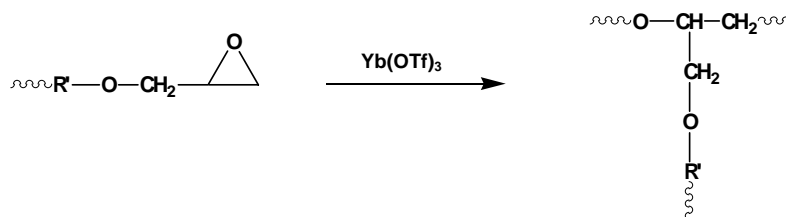
Scheme 2

ted (Scheme 2): a) reaction of SOE

with epoxy groups, b) homopolymer-rization of SOE and c) homopolymer-rization of epoxy groups. Both processes a) and b) lead to the formation of linear ether-ester moieties whereas reaction c) only leads to ether linkages.

To study the combined effect of introducing silicon and phosphorus together we have prepared samples with different compositions which are listed in Table 1.

The crosslinking was studied by dynamic DSC. Figure 1 shows the calorimetric curves for the curing of different mixtures. In the same figure is indicated the P and Si content by means of subscripts (% weight). The crosslinking exotherms of DGEBA, SOE-Si and SOE-iso has been included for the purpose of comparison. As can be seen both SOEs have a low enthalpy as is reported in previous works,[27,28] but their reactivity is different, as show their crosslinking exotherms, being more reactive the silicon-free SOE. The crosslinking exotherms of the mixtures shift to higher

temperatures as silicon content increases probably due to the higher reaction temperature of SOE-Si. In Table 1 the temperatures of the maximum of the exotherms and the enthalpies are collected. As can be seen the enthalpies per epoxy equivalent decreases as the phos-phorus content increases. This could be attributed to the incomplete reaction of diglycidyl compounds, especially in the case of DOPO-BQ-Gly which must melts (about 150 ºC) before reacting, whereas DGEBA is liquid and facilitates the reaction with SOEs at lower temperatures.

To confirm the reaction of SOEs and glycidyl compounds we recorded the FTIR spectra before and after crosslinking. On polymerizing, a new band of carbonyl of linear ester group formed must appear at 1735-1750 cm^{-1}, but in the mixtures that contains SOE-Si a band at 1737 cm^{-1}, due to its ester group, overlaps with the band of linear ester moieties, and therefore only an increase of this band was
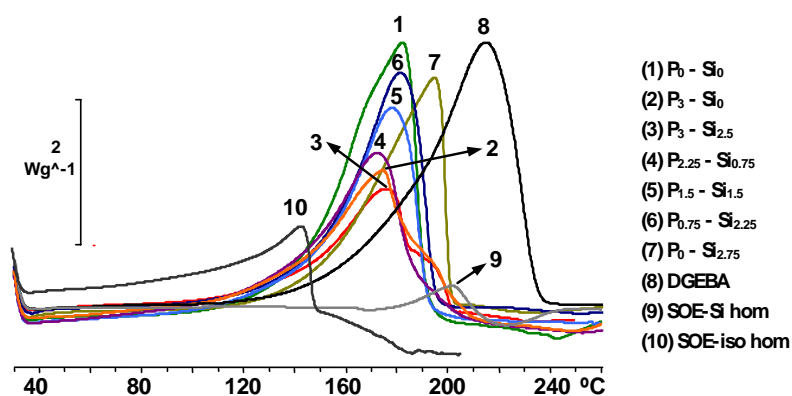

Figure 1. Dynamic DSC plots of different composition mixtures of 2:1 (mol:mol) (DGEBA/DOPO-BQ-Gly):(SOE-Si/SOE-iso), DGEBA and, SOEs initiated by 1 phr of Yb(OTf)$_3$ obtained at 10 ºC/min heating rate.

Legend in figure:

(1) P$_0$ - Si$_0$
(2) P$_3$ - Si$_0$
(3) P$_3$ - Si$_{2.5}$
(4) P$_{2.25}$ - Si$_{0.75}$
(5) P$_{1.5}$ - Si$_{1.5}$
(6) P$_{0.75}$ - Si$_{2.25}$
(7) P$_0$ - Si$_{2.75}$
(8) DGEBA
(9) SOE-Si hom
(10) SOE-iso hom

Table 2. DMA results of Cured Polymers and Volume Changes upon Crosslinking.

Entry	Tg[a] (ºC)	E'$_{max}$ (ºC)	Tan δ (ºC)	Density (g/cm^3) Mixture	Crosslinked	Volume Change (%)
1	76	79	87	1.186	1.197	0.9
2	111	69/135	75/143	1.199	1.208	0.7
3	77	67/140	82/149	1.198	1.207	0.7
4	72	69/148	76/153	1.196	1.202	0.5
5	71	64/135	73/143	1.194	1.201	0.6
6	66	61	72	1.186	1.196	0.8
7	73	70	78	1.186	1.197	0.9
8	139	144	152	1.158	1.193	3

[a] Obtained by DSC.
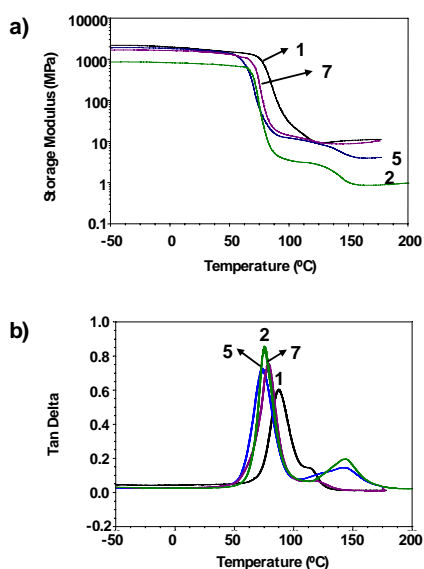
Figure 2. Temperature dependence of Storage Modulus (a), and Tan Delta (b) for 1, 2, 5, 7 cured samples.

observed. The disappearance of the absorption at 916 cm^{-1} due to oxirane ring normally confirms the complete crosslinking reaction, but in this case is difficult to confirm this disappe-arance because it partially overlaps with the band associated to the O-P-Ph moiety of DOPO-BQ-Gly, which appears about 920 cm^{-1} [29].

The dynamic mechanical behavior of the crosslinked materials was obtained as a function of the temperature beginning in the glassy state to the rubbery plateau of each material. Figure 2 depicts the storage modulus (a) and Tan δ (b) of some repre-sentative samples: 1, without P and Si, 2, with only P, 5, with P and Si, and 7, with only Si. All samples showed a degree of non-homogeneity, but it is significant only for P-containing samples which show two maxima in Tan δ and two steps in the storage

modulus. Table 2 collects Tan δ and loss modulus values and the T_g values obtained by DSC are also included. All samples have similar T_gs but lower than pure DEGBA what agrees with the higher distance between knots as consequence of the linear ether-ester moieties introduced by the double ring-opening of SOEs. In the phosphorus-containing samples, the two maxima of Tan δ appear clearly separated. The maximum at lower temperature can be associated to the SOE reaction, alone or with epoxy. The second maximum which corresponds to a more densely crosslinked material, can be associated to the homopolymerization of epoxy, mainly the phosphorus-containing DOPO-BQ-Gly, which needs to reach its melting point before reacting.

The volume changes in the cross-linking reaction of all reactive mixtures were evaluated by density measurements with a Micromeritics gas pycnometer before and after crosslinking (Table 2). The volume change (Δ) was calculated from the following equation:

$$\Delta V\ (\%) = \frac{d_{crosslinked\ polymer} - d_{initial\ mixture}}{d_{initial\ mixture}} \times 100$$

where d is the density.

Sample 8, corresponding to pure DGEBA, show the typical volume shrinkage that generally accompanied the crosslinking reactions.[30]

[a] Temperature of 5% weight loss.
[b] Temperature of the maximum rate of degradation.

Table 3. TGA and LOI results for the Cured Polymers.

Entry	$T_{5\%}$[a] (ºC)		T_{max}[b] (ºC)		Char yield at 800ºC (wt%)		LOI
	N$_2$	Air	N$_2$	Air	N$_2$	Air	
1	271	264	332	334/633	20.4	0.0	19.7
2	262	253	307/404	305/683	17.5	7.0	24.0
3	264	257	326/415	307/639	23.5	10.0	25.4
4	262	261	311/402	315/680	20.9	6.1	23.4
5	265	264	319	314/640	22.1	5.5	22.1
6	276	271	330	330/644	20.5	2.6	21.6
7	266	260	332	321/635	18.0	0.0	20.9
8	314	303	381	360/602	20.4	0.5	20.0

The SOE-containing samples 1-7 show a lower shrinkage (0.5-0.9%). Therefore, it can be concluded that the SOE moieties are effective monomers to obtain crosslinkable copolymers which do not shrink.

at similar temperatures, being slightly lower in air. The introduction of SOEs (sample 1) reduces the stability in comparison to pure DGEBA (sample 8). The
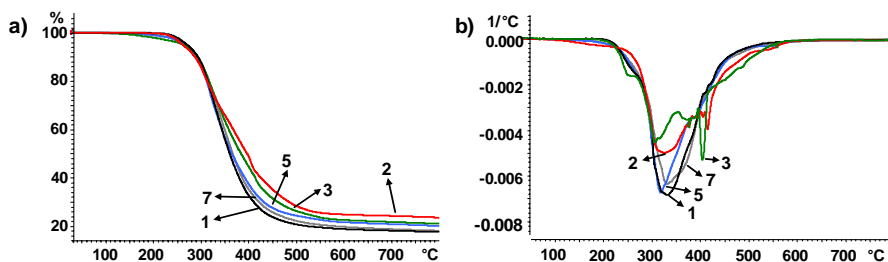

Figure 3. (a) TGA thermograms of samples: 1, 2, 3, 5, and 7 and (b) first derivative under

Thermogravimetric analysis (TGA) is one of the commonly used techniques for rapid evaluation of the thermal stability of different materials. Figure 3 and 4 show the TGA thermograms and DTG curves of some obtained thermosets, from room temperature to 800 °C, in nitrogen and air atmos-phere respectively. Three parameters: temperatures for 5% weight loss, temperatures of the maximum loss rate and char residue at 800 °C, have been used to compare the thermal properties of the cured resins. The values of these parameters are tabulated in Table 3.

Independent on the atmosphere, all the thermosets start the degradation

introduction of Si or P into the reactive mixtures does not decrease the thermal stability respect to the material 1. Thus, the stability dimi-nution must be attributed to the ester groups in the network and not to the presence of Si or P.

In N_2, one or two-stage degradation was observed depending on the composition of the material. Two-stage degradation was detected for the samples that contain higher amount of phosphorus (3 and 2.25 P %wt), what seems to indicate that the second-stage degradation, which does not appear under air, corres-ponds to the phosphorus-containing compound. The char yields slightly increase with the presence of heteroatoms, mainly with P.
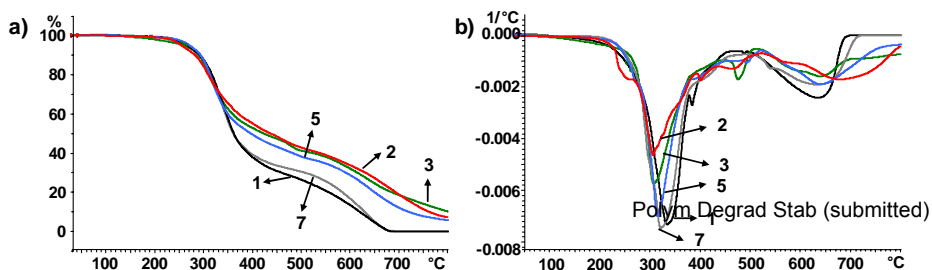

Figure 4. (a) TGA thermograms of samples: 1, 2, 3, 5, and 7 and (b) first derivative under

In air, the degradation initiates at slightly lower temperatures. Moreover, all the samples show at tempera-tures above 600 ºC the typical stage of weight loss, arising from oxidative-degradation. In Figure 4 a) curves 1 (without Si and P) and 7 (with only Si) indicate that the presence of Si slightly increases the stability. By comparison of curves 2 (with only 3% of P) and 3 (with 3% of P and 2.5% of Si) we can observe a higher char yield for 3. The char yield increases with the P content and when Si is also present (sample 3) this increase is greater. Thus, it can be say that phosphorus provided a tendency of char formation and silicon favorably provides thermal stability of char as is previously reported.[12]

The LOI values, which can be taken as indicators to evaluate the polymer's flame retardancy for the materials, were measured and are shown in Table 3. From samples 1 (without Si and P) and 7 (with Si) we observe a slight increase of LOI value for the second. Sample 2 (with P) has a higher LOI value. Thus, based on the similar weight percent, it is noteworthy that phosphorus exhibits a relatively higher flame retardant efficiency than silicon. Whereas small amounts of P are sufficient to increase the LOI value[4,31] it seems that higher amount of silicon are needed to reach a similar effect.[14,32] Sample 3 shows the highest LOI value, as a consequence of both P and Si effect.

CONCLUSIONS

The copolymerization of SOEs and diglycidyl compounds to introduce silicon and phosphorus has been carried out with ytterbium triflate as an initiator. The thermal stability of the materials increases with the introduction of both heteroatoms mainly with phosphorus. Silicon favourably provides thermal stability of char promoted by phosphorus. Small amounts of phosphorus are sufficient to increase the LOI values, but similar amount of silicon only slightly increase the LOI values. The crosslinking of all mixtures take place with low shrinkage, lower than those observed in conventional epoxy resins.

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