

CROSSLINKING OF A POLYACRYLATE BEARING A SPIROORTHOESTER PENDANT GROUP WITH MIXTURES OF DIGLYCIDYL ETHER OF BISPHENOL A AND PHOSPHORUS-CONTAINING GLYCIDYL DERIVATIVES

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Abstract

The cationic crosslinking of a polyacrylate bearing a spiroorthoester pendant group with mixtures of diglycidyl ether of bisphenol A and three phosphorus-containing glycidyl derivatives was carried out with ytterbium triflate as an initiator. The curing process was monitored by Fourier transform infrared spectroscopy. The thermomechanical and thermogravimetric properties were evaluated. The glass transition temperatures of the obtained materials were, in general, above 100 °C. The incorporation of phosphorus into the network increased the limiting oxygen index values, thus improving the flame retardancy of the materials. During crosslinking, all the crosslinked polymers showed slight shrinkage that was much lower than that observed in conventional epoxy resins.

Keywords: cationic polymerization; crosslinking; flame retardance; heteroatom-containing polymers; spiroorthoester; ytterbium triflate

INTRODUCTION

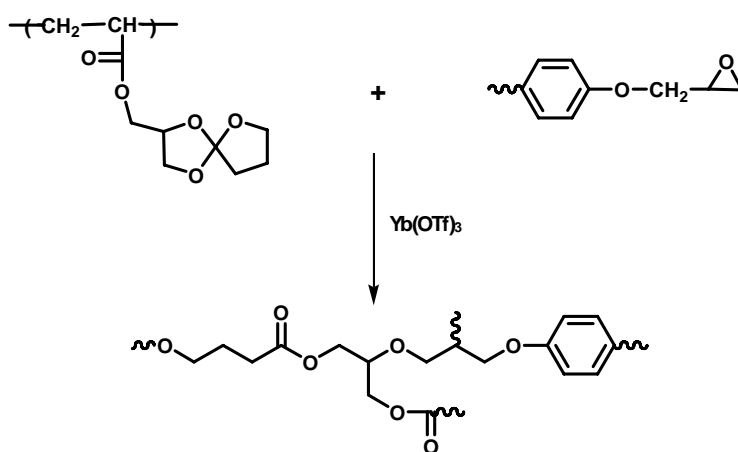
Polymeric networks are extremely versatile materials than can be used

in a wide number of applications. Each application has some require-

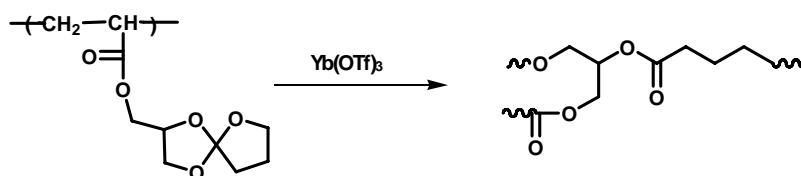
ments that include a combination of physical, mechanical, and other specific properties. Polymer properties depend on the structure of the comonomers, the polymerization mecha-

ners, the polymerization mecha-

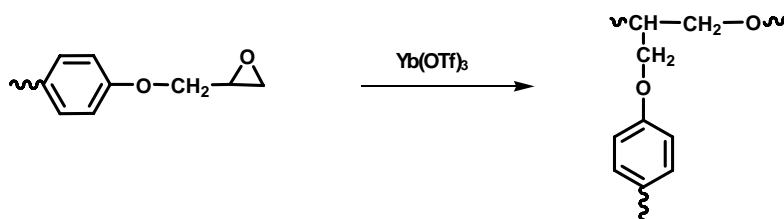
a) Reaction of SOE-AChom with DGEBA



b) Homopolymerization of SOE-AChom



c) Homopolymerization of DGEBA



Scheme 1

nism, and the catalyst used, among others.

In the production of industrial materials, a significant property is the absence of shrinkage upon cross-linking or curing. This shrinkage is a major problem in many industrial applications such as industrial castings, coatings, mold replication, and microelectronics because it leads to poor adhesion to the substrate, delamination, and microvoids and microcracks, which reduce the durability of the materials. Thus, many efforts have been made to reduce the shrinkage. A versatile method for solving this problem is the use of monomers with groups that undergo polymerization with nearly zero shrinkage or even expansion. Some kinds of cyclic monomers have been reported to maintain their volume or actually expand during the double ring-opening polymerization.¹⁻⁵ Among them, spiroorthoesters (SOEs) have a wide variety of structures because they can be prepared from epoxides and lactones.⁶⁻⁸ The polymerization of SOEs bearing a vinyl or acrylate group for radical polymerization has been developed to obtain polymers carrying SOE moieties.^{9,10} Other authors have followed a different strategy and have described the synthesis of polymers carrying SOEs by polymerizing lactone-containing acrylic monomers and the further reaction of the pendant lactones with epoxy compounds.¹¹ The polymers bearing SOEs moieties can be crosslinked, without

significant shrinkage, by cationic double ring-opening polymerization by Lewis acid catalysts.

It has been reported¹²⁻¹⁵ that in the cationic copolymerization of lactones with glycidyl compounds, an inter-mediate SOE is formed that further polymerizes either itself or with epoxides to form poly(ether-ester) (Scheme 1).

Another problem inherent to organic polymers is their flammability. Improving the flame retardancy of organic polymers is a matter of mounting concern and importance given the fact that they are increasingly being used in materials in both domestic and public environments. The flammability of common epoxy systems is a disadvantage in their applications. The epoxy resins in use are mainly the diglycidyl ether of bisphenol A (DGEBA) and tetrabromobisphenol A. However, the bromine-containing epoxy resins release hydrogen bromide, dibenzo-*p*-dioxin, and dibenzofuran during combustion, which cause corrosion and toxicity. Organophosphorus compounds have demonstrated better ability than halogen-containing compounds as flame retardants for polymeric materials by forming a carbonaceous char, which acts as a physical barrier to heat transfer from the flame to the polymer and diffusion of combustible gas and smoke.¹⁶⁻¹⁹

Various phosphorus-containing diglycidyl ether compounds have

been synthesized from phosphoric, phosphonic, or phosphinic acids; therefore, they contain less stable P-O-C bonds.²⁰ In recent years, some diglycidyl compounds have been synthesized from bulky and rigid, phosphorus-containing, reactive 9,10-dihydro-9-oxa-10-phosphaphenan-trene-10-oxide (DOPO).²¹⁻²⁴ All these aryl phosphinate compounds contain P-O-C bonds but show unusually high thermal stability. This stability has been attributed to the O=P-O group being protected by phenylene groups. In a previous work,²⁵ we synthesized a novel glycidyl phosphinate, 9-(9,10-dihydro-9-oxa-10-phosphaphenan-threne-10-oxide)-2,3-epoxy propyl (DOPO-Gly), in which the glycidyl group was directly attached to the P atom. In our search for new phosphorus-containing glycidyls with high thermal and chemical stability without P-O bonds, we also considered phosphine oxides. The nature of this group improves the flammability properties in thermosets, whereas the polarity of the bond increases the hydrogen-bonding ability of the resulting material, possibly improving network adhesion to various substrates.^{26,27} Therefore, we also synthesized isobutyl bis(glycidyl propyl ether) phosphine oxide (IHPO-Gly).²⁸

The aim of this work was to reduce together the aforementioned disadvantages by means of the cationic crosslinking of a polyacrylate bearing an SOE pendant group

[poly(1,4,6-trioxaspiro[4,4]-2-nonylmethyl acrylate) (SOE-AChom) with mixtures of DGEBA and three phosphorus-containing glycidyl derivatives.

The cationic crosslinking was carried out with ytterbium triflate as an initiator, which has been shown to be effective at polymerizing glycidyl compounds and SOEs.²⁹ This crosslinking was studied with differential scanning calorimetry (DSC) and Fourier transform infrared (FTIR) spectroscopy. The materials were characterized with DSC and thermo-gravimetric analysis (TGA). The volume change was evaluated with a Micromeritics gas pycnometer, and the flame retardancy was tested by limiting oxygen index (LOI) measurements.

EXPERIMENTAL

Materials

SOE-AChom⁹

Epibromohydrin (Fluka), γ -butirolactone (Aldrich), boron trifluoride diethyl etherate (Aldrich), triethylamine (Fluka), acrylic acid (Aldrich), 1,8-diazabicyclo[5.4.0]-undec-7-ene (DBU) (Aldrich), and 3-*tert*-butyl-4-hidroxy-5-methylphenyl sulfide (Aldrich) were used as received. 2,2'-Azobisisobutyronitrile (AIBN; Aldrich) was recrystallized from methanol before use.

DOPO-Gly²⁵

Table 1. Compositions (mol %) of the SOE-AChom/Epoxy monomers and curing cycles

Commercial DOPO was donated by Aismalibar. *m*-Chloroperbenzoic acid (MCPBA; Fluka), allyl bromide (Aldrich), epichlorohydrin (EPC;

phate (Aldrich) were used as received.

DGEBA (Epikote resin 827) was acquired from Shell Chemicals

Assay	Composition	Monomer Feed Ratio (mol %) SOE-AChom/DGEBA/Monomer P (wt% P)	Cured		Postcured	
			T (°C)	t (h)	T (°C)	t (h)
1	SOE-AChom/DGEBA	33/67/0 (0%)	100	2	140	5
2	SOE-AChom/DGEBA/DOPO-Gly	33/39.5/27.5 (3%)	100	2	140	5
3	SOE-AChom/DGEBA/DOPO-BQ-Gly	33/34/33 (3%)	100	2	140	4
4	SOE-AChom/DGEBA/IHPO-Gly	33/38/29 (3%)	100	2	160	6

Fluka), potassium carbonate (Panreac), and benzyltrimethylammonium chloride (BTMA; Fluka) were used as received.

10-(2',5'-Bis(glycidyoxy)phenyl)-9,10-dihydro - 9 - oxa-10-phosphaphenanthrene-10-oxide (DOPO-BQ-Gly)³⁰

DOPO, 1,4-benzoquinone (Aldrich), EPC (Fluka), and BTMA (Fluka) were used as received.

IHPO-Gly²⁸

Isobutyl bis(hydroxypropyl) phosphine oxide (IHPO) was kindly supplied by Cytec Canada, Inc. (trade name Cygard RF1243); EPC (Fluka) and tetrabutylammonium hydrogen sul-

(epoxy equivalent = 182.08). Ytterbium (III) trifluoromethanesulfonate [Yb(OTf)₃; Aldrich] was used as received.

All solvents were purified by standard procedures.

Crosslinking Reaction

The epoxy monomers and SOE-AChom in a molar ratio 2:1 were polymerized with 1 phr ytterbium triflate (1 phr = 1 part per 100 parts of mixture weight/weight). Sample bars for dynamomechanical analysis, thermogravimetric analysis, and burn testing were cured in aluminium molds by heating. The prepared epoxy monomers/SOE-AChom mixtures and the curing cycles determined from DSC data, are listed in Table 1.

Instrumentation

The molecular weight distribution of the polymer was determined with a Waters gel permeation chromatograph equipped with a Waters 510 differential RI detector (RID-6A from Shimadzu). The gel permeation chromatograph was operated with three Waters Shodex columns (K80M, Gel 5- μ Mixed-D, Gel 3- μ Mixed-E) at a nominal flow rate of 1 mL/min and a sample concentration of 0.1% in THF as the solvent. Monodisperse polystyrene standards were purchased from Polymer Laboratories for instrument calibration.

Crosslinked studies were carried out on a Mettler DSC-821e thermal analyzer in covered Al pans under N_2 at a scanning rate of 10 °C/min. The determination of the glass transition temperatures (T_g 's) were carried out on a Mettler DSC-822e thermal analyzer in covered Al pans under N_2 at scanning rates of 20 °C/min.

The isothermal polymerization process was monitored with a FTIR-680 Plus spectrophotometer with a resolution of 4 cm^{-1} in the absorbance mode. An attenuated total reflection (ATR) accessory with thermal control and a diamond crystal was used to determine FTIR/ATR spectra.

TGA was carried out with a Mettler TGA/SDTA 851e thermobalance. Cured samples with an approximate mass of 8 mg were degraded

between 30 and 800 °C at a heating rate of 10 °C/min under nitrogen and under air.

The mechanical properties were measured with a dynamic mechanical thermal analyzer (TA DMA 2928). Samples with dimensions of 3 mm x 5 mm x 10 mm were tested in a three-point-bending clamp from -30°C to 190 °C with a heating rate of 3 °C/min and at a fixed frequency of 1 Hz.

The densities of the materials were measured with a Micrometrics Accu-*pyc* 1330 TC gas pycnometer at 30 °C.

LOIs were measured on a Fire Testing Technology flammability unit in conformance with ASTM D 2863 on samples measuring 100 mm x 6 mm x 3 mm.

Scanning electron microscopy (SEM) was performed on a JEOL JSM 6400 scanning electron microscope at an activation voltage of 8 kV. For the atomic mapping, an Oxford INCA energy-dispersive X-Ray microanalyzer was used.

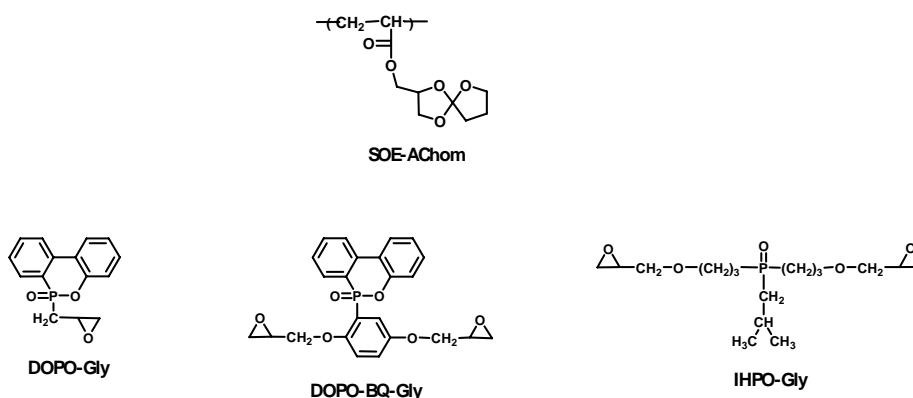
RESULTS AND DISCUSSION

First, we synthesized the starting polyacrylate bearing a SOE (SOE-AChom) with an M_w of 25.000 and the phosphorus-containing glycidyl compounds (Scheme 2). SOE-AChom was synthesized as

previously described⁶ from the corresponding acrylic monomer SOE-AC in benzene using AIBN as a radical initiator, and as phosphorus-containing monomers, we used the three glycidyl compounds shown in scheme 2.

mixture of sodium hydroxide and EPC with tetrabutylammonium hydrogen sulfate as catalyst.²⁸

The cationic crosslinking of SOE-AChom with mixtures of DGEBA and phosphorus-containing glycidyl derivatives was initiated by



Scheme 2

The synthesis of these glycidyl compounds was carried out in different ways. In the case of DOPO-Gly, the glycidyl phosphinate was obtained from DOPO and allyl bromide and further epoxidation of the double bond with MCPBA because the direct reaction of EPC with the active hydrogen atom of DOPO led to an allylic alcohol through an isomerization reaction.²⁵ For DOPO-BQ-Gly, the first step was the reaction of benzoquinone with DOPO,³⁰ and this was followed by the reaction of the two phenolic groups with EPC in excess and BTMA as a catalyst.³¹ The third monomer, IHPO-Gly, was synthesized from commercial IHPO in a

ytterbium triflate. Because of the cationic character of ytterbium triflate, which is similar to boron trifluoride mono ethylamine, in addition to the reaction of SOE with epoxy groups [Scheme 1(a)], other simultaneous processes are expected: the homopolymerization of SOE [Scheme 1(b)], and the homopolymerization of epoxy group [Scheme 1(c)]. The two first reactions give linear poly(ether-ester) structures, and the third lead to polyether chains.²⁹

To obtain the final thermosets containing about 3% phosphorous, mixtures of DGEBA with each phosphorus-containing glycidyl mo-

nomer and 1 phr ytterbium triflate were prepared and used to crosslink SOE-AChom. In this type of copolymerization, the diglycidyl mo-nomers are tetrafunctional, whereas SOE is bifunctional. Therefore, a higher proportion of the former leads to a more densely crosslinked network, whereas a higher proportion of SOE leads to a longer linear chain between crosslinks. The compositions of the samples and the cured and postcured conditions are summarized in Table 1. In all samples, the epoxy/SOE molar ratio was 2/1 to introduce aromatic moieties capable of increasing the T_g values. For comparison, the crosslinking of SOE-AChom/DGEBA was also carried out, and it is included in the same table. After isothermal curing in an oven, a DSC run showed complete cross-

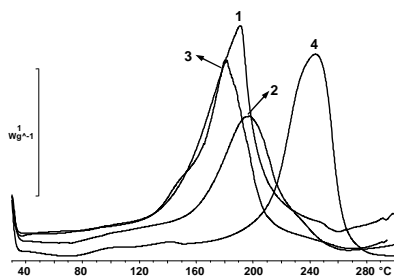
linking because no residual enthalpy was detected.

Figure 1 shows the dynamic DSC plots of all mixtures. As can be seen from the crosslinking exotherms, the temperatures of the maximum, about 190 °C, are similar for samples 1, 2 and 3, but for the sample 4, the maximum of the exotherm appears at a higher temperature, indicating its lower reactivity. The DSC data are listed in Table 2. The enthalpies per epoxy equivalent were calculated because the enthalpy evolved in the SOE ring opening is much lower than for the oxirane ring opening.²⁹ These values were similar for all the samples, though slightly higher for those with phosphorus. The T_g values were calculated after complete curing, by means of a second scan, as the temperature of

Table 2. Calorimetric Data for the Different 1/2 (mol/mol) SOE-AChom/Epoxy Mixtures Initiated by 1 phr Ytterbium Triflate

Assay	ΔH (J/g)	ΔH (KJ/ee)	T_{max} (°C) ^a	T_g (°C)	E'_{max} (°C) ^b	Tan δ (°C)
1	374.7	89.1	191	106	102	113
2	350.7	96.3	197	104	76	89
3	362.4	92.6	182	132	109	135

^a Temperature of the maximum heat release rate.
^b Maximum loss modulus.



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Figure 1. DSC plots of the different 1/2 (mol/mol) SOE-AChom/epoxy mixtures containing 1 phr ytterbium triflate over the temperature range of 30-300 °C at heating rate of 10 °C/min.

the half-way point of the jump in the heat capacity when the material changed from the glassy state to the rubbery state, and they are also collected in Table 2. The lowest T_g

value of sample 4 can be related to the aliphatic structure of IHPO-Gly derivative, which confers a greater flexibility to the network.

FTIR spectroscopy allowed to follow the variation of the groups involved in the crosslinking process. Figure 2 depicts the spectra of the initial mixture, after 1 h at 100 °C, and the final material. We can see the disappearance of the absorption at 915 cm⁻¹ due to oxirane ring, thus confirming that the glycidyl compounds have reacted. A SOE reaction can be observed by the appearance of carbonyl absorption of double ring-opening. In our case,

To study the different processes that occur during crosslinking, we calculated the conversion of epoxy and SOE groups by means the evolution of the bands at 915 cm⁻¹ and 1735 cm⁻¹, respectively. The absorbances were calculated in terms of the peak areas. The conversions of the epoxy and SOE groups were determined by the Lambert-Beer law from the normalized changes in the absorbance with respect to the band at 1606 cm⁻¹ corresponding to the phenyl group in DGEBA, and

$$\alpha_{SOE} = \left(\frac{\overline{A}_{1735}^t}{\overline{A}_{1735}^0} \right)$$

$$\overline{A}_{1735}^t = \frac{A_{1735}^t}{A_{1606}^t} - \frac{A_{1735}^0}{A_{1606}^0} \quad \overline{A}_{1735}^0 = \frac{A_{1735}^0}{A_{1606}^0} - \frac{A_{1735}^0}{A_{1606}^0}$$

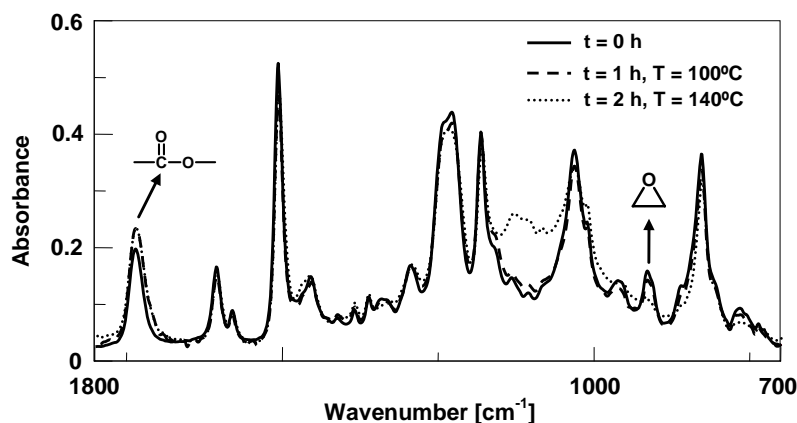
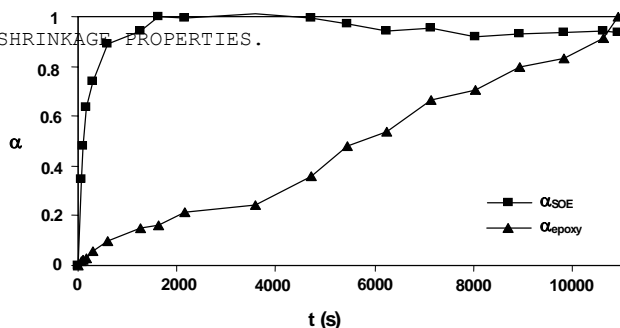


Figure 2. FTIR spectra of a 1/2 (mol/mol) SOE-AChom/DGEBA mixture with 1 phr of ytterbium triflate before heating, after 1 h at 100 °C, and after 2 h at 140 °C.

as the initial polymer has an ester group, this band appears in the initial spectrum, but an increase of this band was observed during crosslinking. This increase is related to the SOE polymerization.

$$\alpha_{epoxy} = 1 - \left(\frac{\overline{A}_{915}^t}{\overline{A}_{915}^0} \right)$$

$$\overline{A}_{915}^t = \frac{A_{915}^t}{A_{1606}^t} \quad \overline{A}_{915}^0 = \frac{A_{915}^0}{A_{1606}^0}$$



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the conversions were calculated with the following equations:

where α_{epoxy} is the epoxy conversion and α_{SOE} is the SOE conversion.

Figure 3 shows the conversions versus the time. The SOE group reacts very fast at the beginning of the process up to a conversion of about 0.7 and reaches a total conversion below 2000 s at 100 °C. After 1 h, the temperature rises to 140 °C, and a decrease in the carbonyl band at 1735 cm^{-1} indicates a slight disappearance of the linear ester that could be related to a depolymerization process or to the beginning of the ester breaking which can initiate the sun-ray crosslinking reactions. On the other hand, the evolution of the epoxy group steadily progresses up to the complete reaction. In the first stages of the crosslinking, when SOE is present in the mixture reaction, process a in Scheme 1 must be the more significant, and then, when SOE is run out, predominantly process c occurs. Process b should occur at the end of the reaction because in previous studies we have observed that this is the process less favored.²⁹

Assay	Density (d^{30} , g/cm^3)		Volume Change (%)
	Mixture	Crosslinked	
1	1.1886	1.1950	0.5
2	1.2147	1.2214	0.6
3	1.2153	1.2172	0.2
4	1.1942	1.2030	0.7

The dynamic mechanical behavior of the crosslinked material was obtained as a function of the temperature from the glassy state of each composition to the rubbery plateau of each material (Figure 4). The crosslinking density of a polymer can be estimated from the plateau of the elastic modulus in the rubbery state.³² However, this theory is strictly valid only for lightly crosslinked materials and is therefore used only to make qualitative comparisons of the level of crosslinking among the various polymers. As can be seen, the incorporation of phosphorus-containing glycidyl compounds into the feed mixture reduces the

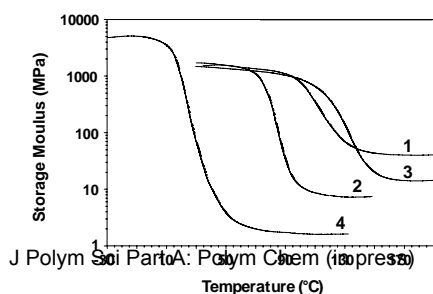


Figure 4. Storage modulus as a function of the temperature of the different thermosets obtained by the copolymerization of 1/2 (mol/mol) SOE-AChom/epoxy mixtures initiated by 1 phr ytterbium triflate.

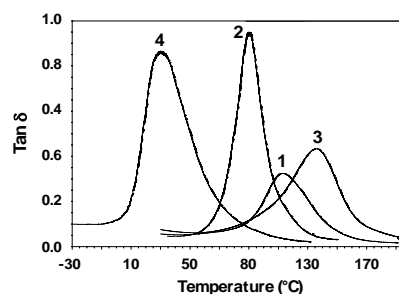


Figure 5. $\text{Tan } \delta$ as a function of the temperature for the different thermosets obtained by the copolymerization of 1/2 (mol/mol) SOE-AChom/epoxy mixtures initiated by 1 phr ytterbium triflate.

crosslinking density, especially in the case of aliphatic IHPO-Gly (curve 4), which enlarges the distance between knots and leads to looser networks. Sample 2 shows a lower crosslinking density than sample 3, and this may be due to the presence of a lower ratio of epoxy groups because DOPO-Gly contains only an epoxy group per mole.

The T_g 's of the crosslinked materials can be detected as the maxima of the loss modulus (E'') and loss factor ($\tan \delta$). Figure 5 shows the plots of the $\tan \delta$ versus the temperature, and Table 2 shows the values of both measurements. The lowest T_g corresponds to sample 4, which contains the more aliphatic moieties. Sample 2 shows a lower T_g value than samples 1 and 3, and this may be due to its lower crosslinking density. Moreover, the analysis of the height and width of the $\tan \delta$ shows trends in the crosslinking densities and network homogeneities as the composition of the material changes. The height of the $\tan \delta$ peak is associated with the crosslinking density. Because $\tan \delta$ is the ratio of viscous components to elastic components, it can be assumed that the decreasing height is associated with lower segmental mobility and fewer relaxing species and therefore indicates that the networks for the DGEBA-rich samples are tighter. The peak width

at half-height broadens as the number of branching modes increases, and this produces a wider distribution of structures. The range of temperatures at which the different network segments gain mobility therefore increases. In our case, there were no significant differences among the samples, and this showed similar branching distributions for all of them. Moreover, all the samples showed unimodal curves indicating their homogeneity.

It has been reported that cationic-double ring-opened SOE-based materials exhibit almost no shrinkage and that copolymers having SOE moieties will also crosslink without shrinkage.

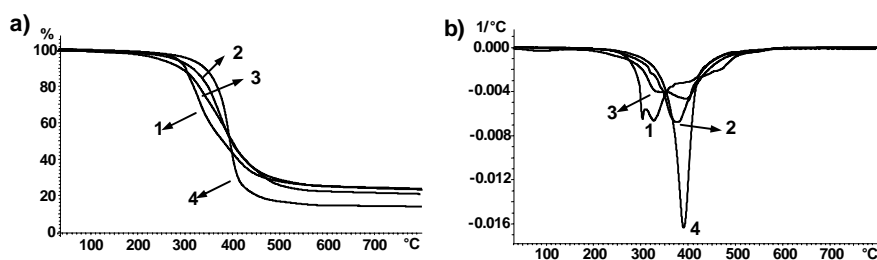


Figure 6. (a) TGA thermograms and (b) first derivatives of the different thermosets obtained by copolymerization of 1/2 (mol/mol) SOE-AChom/epoxy mixtures under N_2 .

Therefore, the volume changes (Δ) in the crosslinking reaction of the copolymers containing SOE moieties were evaluated by density measurements with a Micro-meritics gas pycnometer before and after crosslinking (Table 3). Δ was calculated from the following equation:

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

where $d_{\text{crosslinked polymer}}$ is the density of the crosslinked polymer and $d_{\text{linear polymer}}$ is the density of the linear polymer. Thus, negative values indicate expansion.

Although typical crosslinking of epoxy resins is generally accompanied by significant

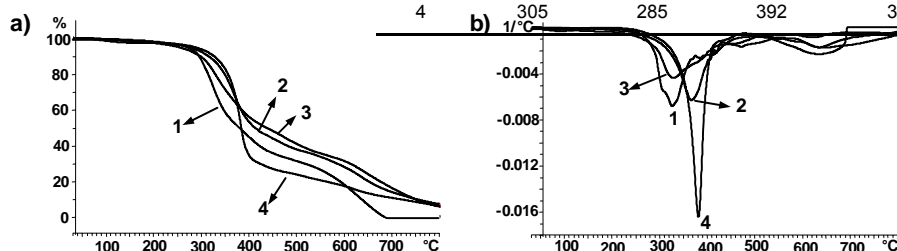


Figure 7. (a) TGA thermograms and (b) first derivatives of the different thermosets obtained by copolymerization of 1/2 (mol/mol) SOE-AChom/epoxy mixtures under air.

volume shrinkage (>3%, depending on the crosslinking mechanism),^{2,33} in all studied mixtures of glycidyl compounds with SOEs, the observed positive values of Δ , between 0.2 and 0.7, are much lower than those observed in the crosslinking of pure DGEBA with ytterbium triflate (ca. 3%).^{29,34} This lower shrinkage on curing must be attributed to the expanding character of SOE moieties. In a previous work,⁹ the crosslinking of the SOE-AC homopolymer initiated by ytterbium triflate was carried out, and it took place with expansion ($\Delta = -3$), but the obtained material

presented a low T_g . The introduction of glycidyl compound in the network increases the T_g values but reduces the expansion produced by SOEs because the homopolymerization of epoxy groups takes place with

Assay	Temperature of 5% Weight Loss (°C)		T_{max} (°C) ^a		Char Yield at 800°C (wt %)		LOI
	N ₂	Air	N ₂	Air	N ₂	Air	
1	279	278	302/326	325/632	23.0	0.3	22.5
2	285	273	373	364	21.4	7.3	24.0
3	240	250	331/394	331	23.5	5.8	25.4
4	305	285	392	380	13.7	6.0	24.1

shrinkage.

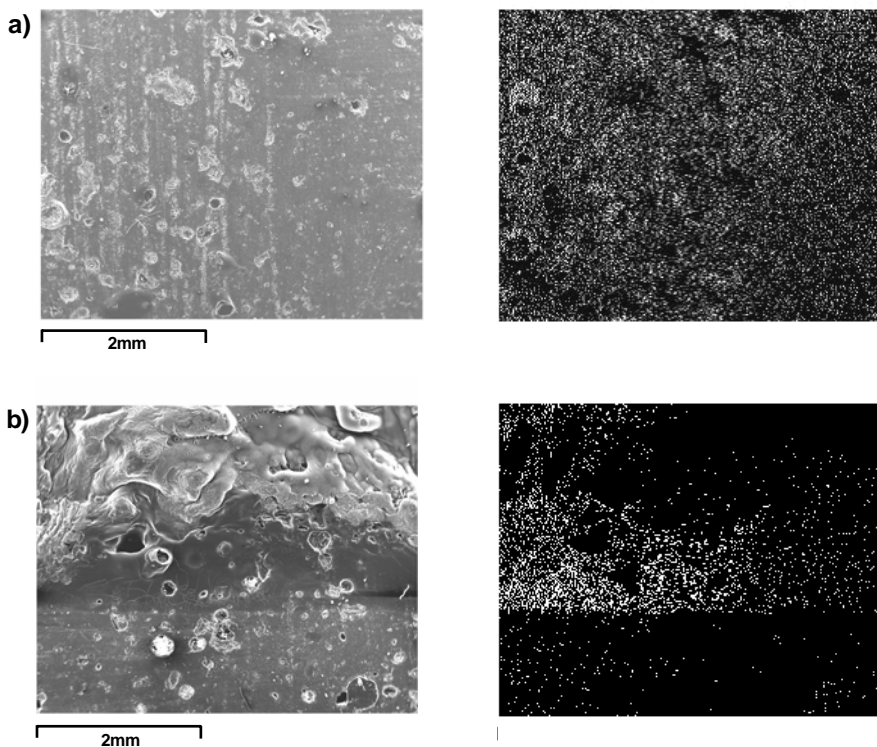
To examine the effect of phosphorous content on thermal stability and the decomposition behaviour, TGA data under nitrogen and air atmospheres were determined and analyzed. Figures 6 and 7 show the weight loss with the temperature for the epoxy compositions as well as the derivative curves under nitrogen and air, respectively. Table 4 summarizes the thermogravimetric data.

In both nitrogen and air atmospheres, only sample 4 has a

single major break in its decomposition curve, which indicates a single decomposition step. However, the other three samples show a more complex decomposition processes. The temperatures of 5% weight loss are about 300 °C, except for sample 3, which begins its degradation at a lower temperature.

In air, a second stage of weight loss for the sample 1, without phosphorus, corresponds to thermooxidative degradation. Under an air atmosphere, a polymeric material at high temperatures loss weight because the char forms is oxidized. This behaviour is in accordance with the mechanism of improved fire performance via phosphorous modification. In this retarded-degradation phenomenon, the phosphorous groups form an insulating protective layer, which prevents the combustible gases from transferring to the surface of the materials, increases the thermal stability at higher temperatures, and improves the fire resistance.

The char yield under nitrogen is correlated to the polymer's flame retardancy,³⁵ but it should be pointed out that, in our case, the experimental char yields of the



phosphorus-containing resins and the phosphorus-free resins are not significantly different under nitrogen. However, under air, the char yield is significantly lower in sample 1 without phosphorus.

The LOI values, which can be taken as indicator to evaluate the polymer's flame retardancy for the phosphorus-containing resins, were measured and are shown in Table 4. The presence of phosphorus increases the LOI values even though the phosphorus content is

Figure 8. SEM and SEM-EDX P mapping micrographs of sample 3 (a) before and (b) after the

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low (ca. 3%), and no significant differences can be observed among the different phosphorus-containing samples.

To better understand the role of phosphorous in the flame retardant properties of the polymer, the element mapping was performed with energy-dispersive X-ray spectroscopy (EDX) on the surfaces of the initial sample and the sample after the LOI test. P mapping of the initial sample 3 indicated a homogeneous distribution of this element, as can be observed in the micrograph on the right of Figure 8(a). The white points in the figure denote P atoms. Figure 8(b) shows the SEM micrograph of the top surface view of the sample after the LOI test. The burned zone has the appearance of a black, charred material with small cavities. The P distribution, on the right of Figure 8(b), shows that the phosphorus density increased towards the top burned surface and that a phosphorus-rich layer formed.

CONCLUSIONS

A polyacrylate bearing a SOE pendant group was crosslinked with mixtures of DGEBA and different phosphorus-containing glycidyl compounds. The T_g values of the obtained materials were above 100 °C, except for the more aliphatic diglycidyl compound. The incorporation of phosphorus into the network increased the LOI values, thus improving the flame retardance

of materials. After crosslinking, all the crosslinked polymers showed slight shrinkage that was much lower than that observed in conventional epoxy resins.

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