

A New Strategy for Controlling Shrinkage of DGEBA Resins Cured by Cationic Copolymerization with Hydroxyl-Terminated Hyperbranched Polymers and Ytterbium Triflate as an Initiator

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ABSTRACT: We report a novel strategy for preparing epoxy thermosetting systems with low shrinkage and improved flexibility and degradability. Diglycidyl ether of bisphenol A (DGEBA) resin was cured with different proportions of hydroxyl-terminated hyperbranched polymer (HBP), using ytterbium triflate as a cationic initiator. The curing process was studied using differential scanning calorimetry and thermomechanical analysis. Characterization of the resulting materials was evaluated using DSC, thermogravimetric analysis, and dynamic mechanical thermal analysis, and the fracture surface was studied using scanning electron microscopy (SEM). When DGEBA is modi-

fied with HBP, it shows a homogeneous morphology and the HBP is incorporated chemically into the network, because hydroxyl groups can react with epoxides under cationic conditions. Higher proportions of HBP reduce the glass transition temperature (T_g) and thermal stability and increase the flexibility. When the proportion of HBP in the curing mixture is increased, the degree of shrinkage is reduced significantly and expansion can be observed. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 111: 2822–2829, 2009

Key words: epoxy networks; toughness; hyperbranched; shrinkage; cationic polymerization

INTRODUCTION

Epoxy resins are an important class of thermosets that are widely used as high-performance materials in a range of applications including adhesives, matrices for fiber-reinforced composites, surface coatings, and electronic encapsulation.^{1,2} However, glycidyl epoxy resins present some drawbacks such as brittleness and high viscosity,¹ shrinkage during the curing process,³ and low degradability. Degradability is an important parameter when epoxy materials are used in coatings or underfills in microelectronic applications to recover the electronic components at the end of their useful lifespan.⁴

Toughness can be improved by incorporating polymer modifiers into the thermosetting matrix to form biphasic systems with fine morphological

structures. Effective polymer modifiers include elastomers,⁵ thermoplastics,⁶ reactive liquid rubber,⁷ or core-shell particles.⁸ However, this procedure has some drawbacks as it decreases the thermal properties and increases the viscosity and internal stress. HBPs exhibit different properties to the modifiers mentioned earlier, including low entanglement in the solid state,⁹ high solubility in various solvents, and low viscosity.¹⁰ Consequently, many authors^{3,11–13} have used HBPs as toughness agents in epoxy systems, although only a few authors have used them as crosslinking agents.^{14–16} When hydroxyl-terminated HBPs are used in cationic conditions, they are expected to incorporate into the network structure via hydroxyl-induced chain-transfer reactions that occur during the cationic ring-opening polymerization of epoxy groups.^{15–17}

Most of the works in the literature related to epoxy/HBP systems focus on the toughening effect of the HBP and on the improved processability caused by the decrease in viscosity, but not on the shrinkage and internal stress generated during the curing process.^{11,13–15,18,19} Manson et al. proved the toughening effect of the hyperbranched polymers (HBPs) by a phase-separation process. The addition of the hydroxylic hyperbranched modifier

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produces phase-separated morphologies because of the hydroxylic groups do not covalently bond to the network structure because of the primary amine curing agent used in obtaining these materials.¹²

We examine the influence of the hydroxyl-terminated HBP on the shrinkage of the epoxy systems when the HBP is incorporated chemically into the network. Shrinkage during curing is expected to be influenced strongly by the presence of HBP, because the structure of the material is modified.³ The changes produced in the glass transition temperature, which are related to the increase in free volume, and in the intermolecular and intramolecular H-bonds when hydroxyls react with epoxy groups will tend to expand the compact structure of the hyperbranched moiety.²⁰ However, a gradual increase in the density of the cured epoxy materials on adding increasing proportions of hydroxylic HBP was reported in cationic photocuring process.¹⁵

In previous research we used lanthanide triflates as cationic initiators to cure epoxy/lactone mixtures and obtained completely cured materials with inserted linear ester moieties. Lanthanide triflates also remain active even in humid environments and in air atmosphere.^{21,22} The copolymerization reaction between epoxy resins and lactones led to an increased distance between crosslinks and to the introduction of flexible chains and therefore to less fragile materials. Linear esters can be thermally broken by a β -elimination mechanism, so it was possible to obtain more highly degradable thermosets with potentially reworkable properties.²³ This procedure also reduced the generation of internal stresses because of the higher conversion reached at gelation, and led to the *in situ* formation of expandable spiroorthoesters as intermediates.^{24,25}

The aim of the research reported here was to obtain and characterize new epoxy-based materials with improved flexibility, degradability and shrinkage. We copolymerized a diglycidyl ether of bisphenol A (DGEBA) with hydroxyl-terminated hyperbranched polyester (BOLTORN H30) using ytterbium (III) trifluoromethanesulfonate as an initiator. We obtained novel epoxy/HBP thermosets with enhanced properties in which the hyperbranched polyester was incorporated chemically into the network via cationic ring-opening polymerization. To the best of our knowledge, this is the first time that expansion has been reported in the copolymerization of an epoxy resin with a hydroxyl-terminated HBP.

EXPERIMENTAL

Materials

Diglycidyl ether of bisphenol A (DGEBA) Epitoke Resin 827 from Shell Chemicals (Rotterdam, Nether-

lands) (epoxy equivalent = 187 g/equiv), ytterbium (III) trifluoromethanesulfonate (99.99%) from Aldrich (Steinheim, Germany), hyperbranched polyester Boltorn H30 (32 terminal hydroxyl groups, 3600 g/mol) from Perstorp (Perstorp, Sweden) were used as received.

Preparation of the curing mixtures

Boltorn H30 in concentrations of 5, 10, 15, and 20% (by weight) was easily dissolved in acetone, and the solution was added to DGEBA. A homogeneous solution was obtained after the solvent was removed under reduced pressure and 1% (by weight) of ytterbium triflate was added. The formulation of pure DGEBA was prepared by adding to the DGEBA 1% (by weight) of ytterbium triflate. Samples were carefully stirred and kept at -20°C before use to prevent polymerization.

Measurements

Calorimetric analyses were carried out on a Mettler DSC-822e calorimeter with a TSO801RO robotic arm. Samples of 10 mg in weight were cured in aluminum pans in a nitrogen atmosphere. Nonisothermal experiments were performed from 0 to 225°C at heating rates of 2, 5, 10, and $15^{\circ}\text{C}/\text{min}$ to determine the reaction heat and the kinetic parameters.²⁴ The T_g of the cured materials was determined in a second scan at $10^{\circ}\text{C}/\text{min}$ after dynamic curing. The T_g of the uncured materials was determined by a similar process to the first.

The isothermal curing process, at 140°C , was monitored with a FTIR Bomem Michelson MB 100 spectrophotometer with a resolution of 4 cm^{-1} in the absorbance mode. An attenuated total reflection accessory with thermal control and a diamond crystal (Golden Gate Heated Single Reflection Diamond ATR, Specac-Teknokroma) was used to determine FTIR spectra. Samples dynamically cured in differential scanning calorimetry (DSC) were also analyzed by FTIR.

The gel point and the shrinkage undergone during curing were determined using a Mettler TMA40 thermomechanical analyser. The samples were supported by two small circular ceramic plates and silanized glass fibers, which were impregnated with the sample. Isothermal experiments at 140°C were performed by applying a periodic force in between 0.0025 and 0.01 N to monitor contraction during the curing process.^{25,26} The gel point was taken as the time at which the amplitude of the oscillations decreased suddenly, which occurred because the gelled material was less deformable. The degree of gel conversion was determined by thermomechanical analysis (TMA) and DSC according to a methodology described previously.²⁶

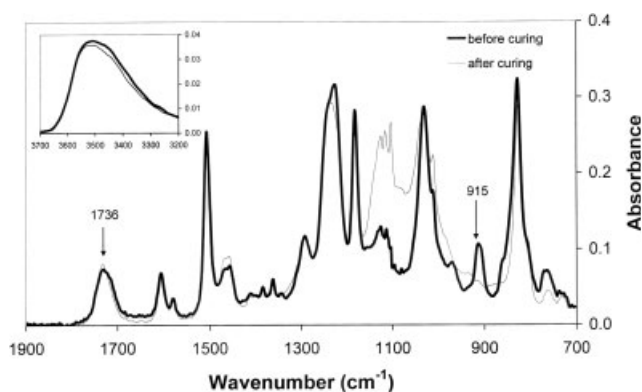


Figure 1 FTIR spectra of DGEBA at 140°C with 10% H30 before and after curing.

Dynamic mechanical thermal analysis (DMTA) was carried out using a Rheometrics MKIII analyser. Prior to analysis, the samples were cured isothermally in a mold at 140°C for 1 h and then subjected to postcuring at 150°C for 2 h. Single cantilever bending at 1 Hz was performed from 0 to 225°C at 2°C/min on prismatic rectangular samples (1.5 × 9 × 5 mm³).

Thermogravimetric analysis (TGA) was carried out in a nitrogen atmosphere with a Mettler-Toledo TGA-50 thermobalance. Cured samples with an approximate mass of 5 mg were degraded between 35 and 600°C at a heating rate of 10°C/min in nitrogen and air atmospheres (200 cm³/min measured in normal conditions).

The density of the samples was measured before curing by the standard procedure of filling a pycnometer with the viscous mixture in a thermostated bath at 30°C. The density of the cured samples was determined indirectly by the flotation method, starting from solutions of KBr with densities that were lower and higher than that of the sample. The shrinkage was calculated from the density measurements of the cured and uncured materials.^{23,24}

The gel content of the cured materials was determined by measuring the weight loss after 24 h of treatment with chloroform at boiling temperature.

A scanning electron microscope (SEM; Jeol JSM 6400) with a resolution of 3.5 nm was used to examine the fracture surface morphology of the samples, which were previously coated with a conductive gold layer.

The kinetic triplet (A , preexponential factor, E , activation energy; and the kinetic model) was determined using integral nonisothermal kinetic analysis combined with the Coats-Redfern method and the reduced master curves procedure. Details of the kinetic methodology are given in previous studies.^{27,28}

RESULTS AND DISCUSSION

We studied the cationic curing of DGEBA with different quantities of a hydroxyl-terminated hyperbranched polyester using ytterbium triflate as initiator to obtain new thermosets with greater degradability and flexibility and with few internal tensions. Figure 1 shows FTIR spectra of the formulation containing 10% of H30 before and after curing, including the changes that the most significant bands undergo. The disappearance of the epoxy band at 915 cm⁻¹ and the increase in the absorbance peak at 1100 cm⁻¹ (C—O—C stretching of aliphatic linear ester) indicates that the epoxy groups have polymerized. The permanence of the H30 carbonyl bands at 1736 and of the hydroxyl bands at 3500 cm⁻¹ indicate that all H30 remains in the formulation after curing. Table I shows the characterization results for the materials obtained. The constant values of the enthalpies per equivalent of epoxy group and their similarity to the values found in the literature for the opening of the epoxy group^{23,29} suggest that the curing process was almost complete for all formulations. Infrared spectroscopy verified that the epoxy groups react

TABLE I
Calorimetric, DMTA, and TGA Data and Gel Content of the Studied Systems

H30 (%)	Eq. initiator/ Eq. epoxy	Gel content (%)	DSC			DMTA		TGA	
			Δh^a (J/g)	Δh^b (kJ/ee)	T_g (°C)	ΔC_p^c (J g/K)	$T_{\tan\delta}^d$ (°C)	T_{onset}^e (°C)	T_{max}^f (°C)
0	0.002936	100	526	95.8	132	0.201	159	275	356
5	0.003120	100	501	96.1	121	0.215	149	268	350
10	0.003294	99	474	95.9	112	0.226	136	255	343
15	0.003487	99	442	94.7	106	0.235	124	233	336
20	0.003708	98	413	94.0	96	0.254	110	205	328

^a Enthalpies per gram of mixture.

^b Enthalpies per equivalent of epoxy group.

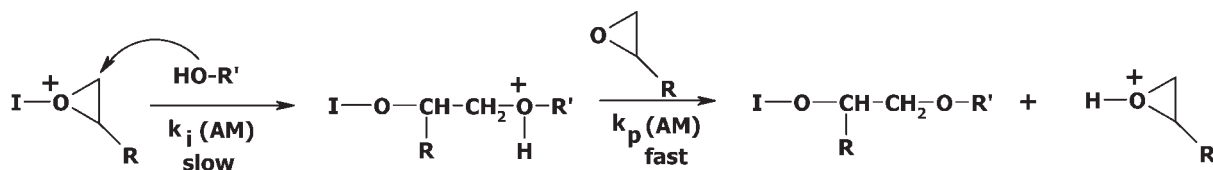
^c Difference in heat capacity when the material changed from glassy to the rubbery state.

^d Temperature of maximum of the $\tan \delta$ at 1 Hz.

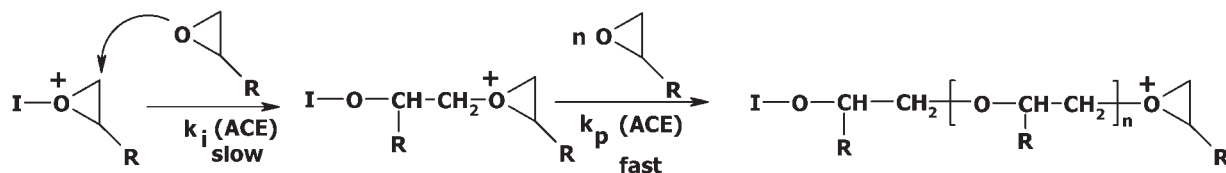
^e Temperature of the onset decomposition on the TGA data at 10°C/min calculated for a 2% weight loss.

^f Temperature of the maximum decomposition rate based on the TGA data at 10°C/min.

Activated monomer mechanism (AM)



Activated chain end mechanism (ACE)



Scheme 1 Activated monomer and activated chain end mechanisms.

completely, showing that absorbance of the oxirane group disappears completely at 915 cm^{-1} (formulations cured dynamically showed similar spectra to those in Fig. 1). The low soluble material content in the cured systems suggests that the hydroxyl groups reacted partially with the epoxy groups and that HBP is chemically incorporated into the network, although the exact quantity of hydroxyl group reacted cannot be determined because when one hydroxyl reacts another one appears. The presence in cationic systems of a HBP with a large number of reactive hydroxyl groups can generate many chain-transfer reactions with epoxides which take place via an activated monomer (AM) mechanism.³⁰ As shown in Scheme 1, the AM mechanism produces a proton-transfer reaction between a hydroxyl group and an activated epoxy group, which prevents subsequent chain growth and generates a new active species and growing chain. In the absence of hydroxyl groups, the cationic epoxy curing only takes place via the active chain-end (ACE) mechanism. In the ACE mechanism, propagation takes place through the reaction of epoxy groups with the active species, which is an oxonium ion at the chain-end. In this case, the reaction generates longer polymer chains and fewer terminal units, so a higher degree of crosslinking can be expected. The decrease in T_g with increasing proportions of H30 is consistent with the lower crosslinking density, which is probably because of the structure of H30, the greater contribution of the AM mechanism, and the plastifying effect of H30 in the epoxy matrix.^{14,15} The systems with larger proportions of H30 contain a higher proportion of these voluminous groups and the chains are shorter, which creates a greater excess of free volume. Consequently, larger quantities of H30 improve the molecular mobility and lower the

glass transition temperature of the polymer. In addition, the increased variation in calorific capacity at T_g , ΔC_p , with larger proportions of H30 that can be related to a lower crosslinking density.³¹ In general, the decrease in T_g with increasing proportions of H30 has a positive influence on the thermal and chemical contraction and the internal tensions. This is because these effects are largely produced during the cooling phase at temperatures below T_g .

Figure 2 shows the conversion curves (%) versus the temperature obtained during the dynamic curing of different samples at $10^\circ\text{C}/\text{min}$ in the DSC experiments. The reaction rate initially decreases as the H30 proportion increases, but it subsequently increases at higher proportions of H30. This result is reflected in the calculated constant rate values shown in Table II. Although the curing rate increases in some systems when HBP is added,^{10,13,15} it can also decrease in the presence of other factors. The curing rate increases with lower viscosity, smaller crosslinking, and larger quantities of initiator

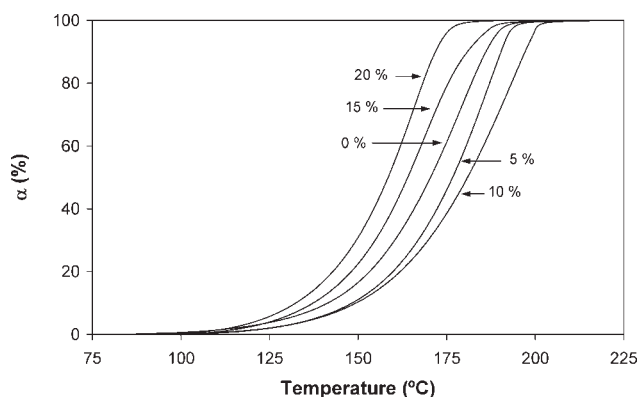


Figure 2 Conversion (%) versus temperature at $10^\circ\text{C}/\text{min}$ for different DGEBA/HBP formulations.

TABLE II
Kinetic Parameters of Curing for the Studied Systems

H30 (%)	E^a (kJ mol ⁻¹)	ln A^b (s ⁻¹)	r^c	$k_{T=140^\circ\text{C}}^d$ (10 ⁴ s ⁻¹)
0	78.4	15.32	0.999	5.51
5	78.2	14.99	0.999	4.20
10	73.2	13.47	0.999	3.93
15	76.2	15.10	0.999	8.84
20	72.7	14.31	0.999	10.54

^a Apparent activation energies determined using isoconversional nonisothermal procedure at a conversion of 0.5.

^b Preexponential factors at a conversion of 0.5 for kinetic model R₂.

^d Linear correlation coefficients.

^c Rate constants at a conversion of 0.5 for kinetic model R₂ determined using Arrhenius equation.

per epoxy group (Table I) when the proportion of H30 increases. However, when the reacting system contains a smaller proportion of epoxy groups it is less likely to form active species through the interaction between the epoxy groups and the initiator. Consequently, the rate of chain propagation is reduced. The reaction rate is also affected by the competition between the propagation mechanisms AM and ACE, and by the possible chemical incorporation of H30 into the network. Previous research showed that the cationic curing of a DGEBA resin took place at a higher rate when an AM mechanism was used than with an ACE mechanism.³² The relative influence of these different factors can accelerate or decelerate the curing process, which can be observed in the system studied here.

Table I shows the results of the thermogravimetric analysis in nitrogen atmosphere. As stated in the introduction, the thermoset must have low thermal stability to produce coatings that can be eliminated at the end of their useful lifespan or repaired if necessary. The onset temperature of degradation, and not the temperature of maximum degradation rate, is the most important thermal parameter for producing a reworkable thermoset, because the fragments created when the three-dimensional network has begun to degrade can be eliminated by dissolution or friction. When the H30 proportion is increased, the thermal stability of the material decreases and the system begins to degrade at lower temperatures, although it remains relatively stable and does not degrade during curing. The high degradability of the material can be attributed to the smaller degree of crosslinking when the proportion of H30 increases and to the addition of ester groups from H30 to the network.^{4,23} Similar results were obtained in air atmosphere although in this case a new degradation step, associated with the burning of the carbon formed during the thermal degradation, appeared at high temperatures. It can be concluded that the

TABLE III
Gelation Data, Densities, and Expansion of the Systems Studied

H30 (%)	t_{gel}^a (min)	α_{gel}^b (%)	ρ_{mon} (g cm ³)	ρ_{pol} (g cm ³)	Expansion ^c (%)
0	12.1	42	1.167	1.193	-2.2
5	20.1	47	1.169	1.174	-0.43
10	22.5	52	1.168	1.122	4.10
15	12.5	55	1.171	1.102	6.26
20	9.5	60	1.174	1.038	13.10

^a Experimental gel time determined using TMA.

^b Conversion at gelation determined using TMA and DSC.

^c Expansion determined as $[-(\rho_{\text{polymer}} - \rho_{\text{monomer}})/\rho_{\text{polymer}}]100$.

degradability of the materials is controlled by the temperature and not by the atmosphere.

Table III shows that higher proportions of H30 reduce the contraction during the curing process and that large quantities of HBP can produce expansion during curing. This finding can be related to the higher compactness of H30 before curing, which is produced by the large number of intermolecular H-bond and intramolecular H-bond interactions. These types of interactions decrease when the terminal hydroxyl groups react with the epoxy groups. The highest decrease is observed in the intramolecular interactions.²⁰ The H30 groups incorporated into the network increase the free volume and reduce the density and the T_g of the cured materials considerably (Tables I and III). The same decrease was observed by Ratna et al., although their study was carried out with an HBP with terminal reacting epoxy groups.³³

Figure 3 shows the dimension changes and the deformability of the material during curing in TMA for the formulation containing 15% of H30. A large expansion can be seen at around 650 s; after this

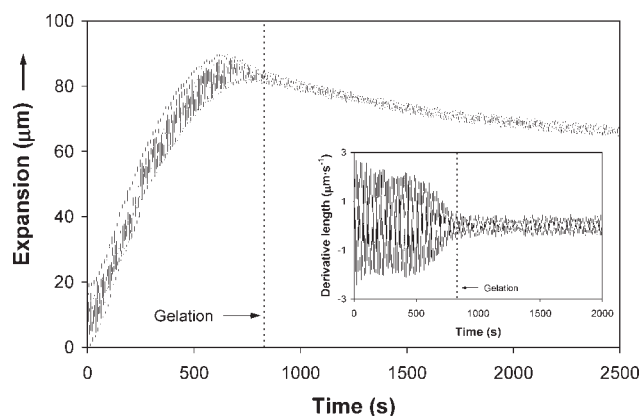


Figure 3 TMA thermogram of isothermal curing of DGEBA at 140°C with 15% of H30. The inset shows derivative length versus time for the same curing process.

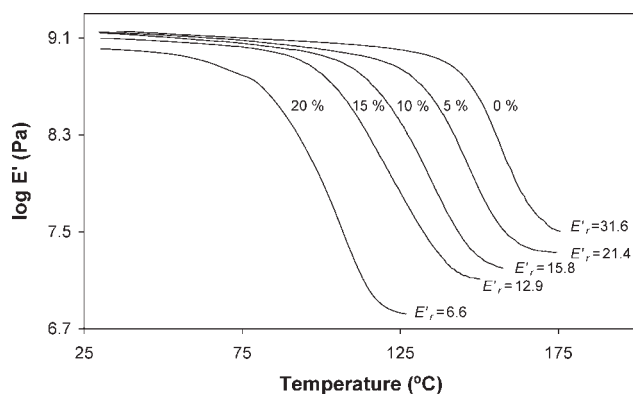


Figure 4 Logarithm of the storage modulus versus temperature at 1 Hz for several DGEBA/HBP formulations. The relaxed modulus, E'_r (MPa), is also shown.

point, the material contracts slightly until the end of the curing process. During the expansion, the compacted H30 groups should be incorporated into the network to produce an excess of free volume that compensates for the contraction associated with the homopolymerization of epoxy groups. This contraction occurs when the chemical incorporation of H30 groups into the network stops. Some authors have found that the addition of HBP reduces the contraction in acrylate and methacrylate systems^{34,35} and the internal tensions produced during curing in epoxy/amine systems.³ However, other authors observed the opposite effect in cationic photocuring processes in epoxy systems.^{15,16} We believe that the expansion observed during the curing process in this study was caused by the chemical incorporation of H30 into the network, the lack of phase separation, and the decrease in T_g as a result of the increase in free volume.

In TMA, gelation is seen as a reduction in the oscillation amplitude because the gelified material is less deformable (Fig. 3). This reduction is better observed in the signal derivative (inset Fig. 3) where the effect of volume change is eliminated. When the H30 proportion in the reactive mixture increases, the material gelifies at higher conversions and the degree of contraction after gelation is reduced (Table III). This effect could be beneficial for the material because the period after gelation is the point at which most internal tensions are generated. The mathematical theory of network formation³⁶ suggests that gelation should occur at lower chemical conversion when a crosslinker with a functionality greater than five is added to the curing mixture. However, it was found that the addition of HBPs to the mixture led to gelations which were consistent with the use of crosslinkers with functionalities of four or less.³⁷ The gelation at higher conversions may have been produced because the effective functionality of H30 ($f \approx 3$, AB₂-type-monomer) is

smaller than that of DGEBA ($f \approx 4$) and because the chain-transfer reactions reduce the crosslinking points and increase the number of groups that must react, which creates an insoluble structure. Table III shows how the gel time increases with H30 content up to a proportion of 10%; at higher proportions, the gel time decreases. This effect can be related to the value of α_{gel} , although it depends mainly on the kinetic changes observed in the curing process (Table I and Fig. 2) when the proportion of H30 is increased.

Figures 4 and 5 show the mechanical relaxation spectra at 1 Hz for the formulations studied. As the proportion of H30 increases, the modulus–temperature curves move towards smaller temperatures and the value of the relaxed modulus, calculated at the temperature $T_g + 40^\circ\text{C}$, decreases dramatically (Fig. 4). Both effects are consistent with the lower value of T_g revealed by DSC and the flexibilizing effect of H30. The maximums of the $\tan \delta$ –temperature curves (Fig. 5 and Table I) also indicate that T_g decreases when the content of HBP is increased, as well as showing only one relaxation peak. The absence of mechanical relaxation at around 30°C (mechanical relaxation of pure H30)¹⁵ suggests that the materials do not present phase separation. Figure 6 shows scanning electron microphotographs of the fracture surfaces of cured DGEBA with and without HBP. The fracture surfaces of the pure and modified DGEBA materials consist of only one phase. The rougher surface seen in the fractographs of the HBP-modified material suggests that the fractured specimens broke slightly more yielding than that the unmodified epoxy network. Therefore, it appears that the addition of HBP improved the fracture properties of cured DGEBA. Since there is no phase separation in the modified DGEBA material, the mechanism of toughness improvement cannot be explained by a phase-separate mechanism^{11,12} and is instead based on *in situ* homogeneous reinforcing

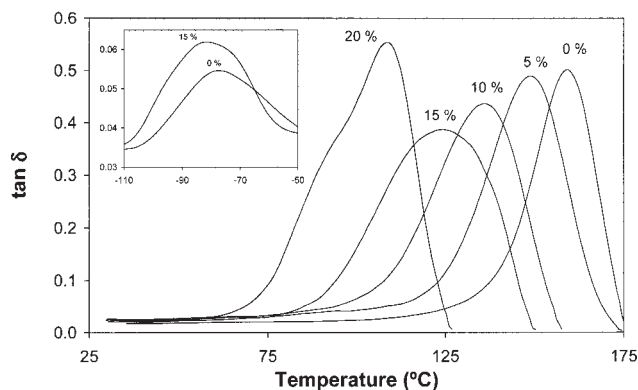


Figure 5 $\tan \delta$ versus temperature at 1 Hz for several DGEBA/HBP formulations. The inset shows traces of $\tan \delta$ versus temperature for the β -relaxation of some cured systems.

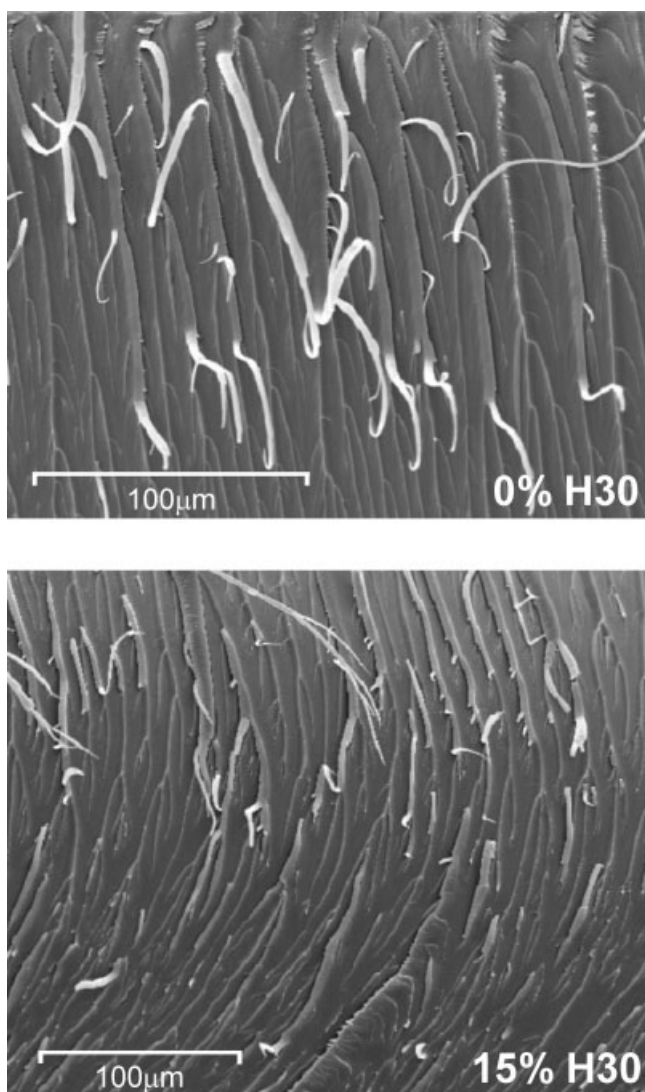


Figure 6 SEM of the fracture surfaces in some cured systems.

and toughening.^{14,38} Some authors attributed the increase in toughness to the plasticization effect of the HBP.³⁹ It is generally accepted that the increase in toughness correlates with the increase in the area of the β -relaxation peak in DMTA experiments.^{14,40} Using this technique, we detected the relaxation at -0°C (see inset, Fig. 5), which can be associated with conformational movements. The relaxation peak area increases with the HBP content in the thermosets, which again confirms that HBP improves the mechanical characteristics of epoxy materials.

CONCLUSIONS

It was demonstrated that lanthanide triflates are effective initiators in the cationic curing of DGEBA/hydroxyl-terminated hyperbranched polyester sys-

tems. During this process, HBP is chemically incorporated into the network via hydroxyl-induced chain-transfer reactions.

New thermosets were prepared without phase separation at the micrometric level and with improved contraction and flexibility properties. The increased flexibility must be produced by an *in situ* homogeneous toughening mechanism and by a plasticizing effect.

H30 reduces the contraction during curing and can even lead to expansion when added in high proportions. This behavior is observed because intermolecular and intramolecular H-bond interactions decrease and the free volume increases when HBP reacts and is incorporated into the network.

Conversion at gelation increases with H30 proportion and the quantity of material that reacts when the system is gelified decreases, which reduces the internal tensions generated in the material.

The network of the materials obtained contains a large number of ester groups, so the materials are more likely to be reworkable.

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