Study of lanthanide triflates as new curing initiators for DGEBA

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Abstract

A new class of cationic initiators, lanthanide triflates, has been studied in the curing of diglycidyl ether of bisphenol-A (DGEBA). The kinetics of this process has been evaluated by the isoconversional method that has been proved as an excellent tool to predict the technical parameters of this process. The thermal stability of the crosslinked materials has been studied by thermogravimetric analysis (TGA) and their mechanical characteristics by dynamomechanic thermal analysis (DMTA). © 2000 Elsevier Science Ltd. All rights reserved.

1. Introduction

Owing to the important commercial utility of polyethers and epoxy networks, the complex mechanism of the cationic ring-opening polymerization of epoxides has been investigated with a special attention [1]. Novel cationic photo and thermic activated initiators have been developed, because in the absence of light or heat no reaction takes place, allowing storage or processing. On exposure to light or heat, decomposition of the initiators provides powerful reactive initiators, which starts the polymerization process leading to polyether chains [2].

In a cationic mechanism there are a number of side reactions that have to be avoided, if a high molecular weight polymer is desired. The most important one is provided by the heteroatoms in the polymer chain that are nucleophiles and can transform the strained active species in the chain ends into unstrained onium ions. This reaction can either be intra- or intermolecular leading to cyclic oligomers or to an increase in the polydispersity.

Of the described cationic initiators, Lewis acids lead to not high degree of polymerization, although it varies to some extent with the nature of the catalyst, either in the cationic center or in the contraion.

Cationic polymerization can lead to a crosslinking process if diepoxides are taken as monomers. Thus, a wide variety of compounds such as $AlCl_3$, $SnCl_4$, $TiCl_4$, $SbCl_5$ or BF_3 can be used catalytically as cationic curing initiators for epoxy resins that act with a fast rate. Moreover, their low initial viscosities and fast curing make them good candidates for a fast reactive processing. Among the above-mentioned Lewis acids, the most common is the borontrifluoride. This catalyst is difficult to handle, gives high exothermic reactions and therefore produces a too rapid gelation. For these reasons it is generally used as a complex with ethers or amines. However, in common with most of the initiators in this class, it has the disadvantage of causing corrosion problems under high humidity environments [3].

Lanthanide triflates serve as Lewis acids and they maintain the catalyst activity even in aqueous solution [4], where usual common Lewis acids decompose or change their activity and now they are commercially available. Moreover, the strong electronwithdrawing capacity of the trifluoromethanesulfonate anion enhances the Lewis acid character of the initiator. Lanthanide ions have low electronegativity and strong oxophilicity, which allows the metal to tightly, coordinate to the oxiranic oxygen. They have large ionic radii and their coordination sphere can be modified leading to a different activity. All these characteristics allow to create template structures in the epoxide network [5].

Lanthanide triflates has been proved as excellent catalysts in the ring opening of oxiranes in the presence of nucleophilic agents such as amines [6,7], indoles [8] or alcohols [9]. Moreover, recently some publications about their use in the polymerization of *p*-methoxystyrene [10], cyclosiloxanes [11] and vinylethers [12] have appeared.

In the present work, we have studied the possibility to use these compounds in the thermal crosslinking process of the

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diglycidyl ether of bisphenol A and their kinetic parameters in order to test their potentiality in industrial applications.

2. Experimental

2.1. Materials

Diglycidylether of Bisphenol A (DGEBA) (epoxy equiv. = 174 g/eq) (ALDRICH) was used as received.

Ytterbium (III), samarium (III), cerium (IV), erbium (III) and dysprosium trifluoromethanesulfonate (ALDRICH) and lanthanum (III) trifluoromethanesulfonate (ALFA AESAR) were used without purification.

Solvents were purified by standard methods.

The samples were prepared by solving DGEBA in methanol and mixing it with the required amount of the selected triflate salt previously dissolved in dichloromethane. This solution was evaporated at room temperature under vacuum.

2.2. Characterization and measurements

Calorimetric studies were carried out on a Mettler DSC-821e thermal analyzer in covered Al pans under N_2, at various heating rates (5–20°C/min). The calorimeter was calibrated using an Indium standard (heat flow calibration) and an Indium–Lead–Zinc standard (temperature calibration). The resin or the mixture of about 5 mg of known weight of the epoxy with the suitable amount of initiator was put into an aluminum pan. The kinetics of curing of the epoxy resins was evaluated using the kinetic software STAR of Mettler–Toledo.

Thermogravimetric analyses were carried out with a Perkin–Elmer TGA-7 system in N_2.

A Rheometrics Instruments dynamic mechanical thermal analyzer (DMTA) PL-DMTA MK3 was used to measure the storage modulus (E') and the loss factor (tan δ) of the cured epoxy samples with a post-cured treatment in an oven at 100°C for 24 h. DMTA was used in single cantilever bending mode, the frequency used was 1 Hz. The prismatic samples had widths varied between 3.9–6.5 mm and support spans of 5 mm. The specimen thicknesses varied between 1.37–3.74 mm. Dynamic scans were performed from −150 to 200°C at a heating rate of 2°C/min.

3. Results and discussion

It is known that initiators have a large influence on the processability, mechanical properties, adhesion, long term stability, reactivity in different chemical/physical environments and even in the total cost of the resulting crosslinked polymers. As has been mentioned above, Lewis acids induce cationic polymerizations leading to homopolymerization reactions, although in general the degrees of polymerization achieved are not high. The lower values of the molecular weight in the polymerization of monoepoxides

have been attributed to equilibrium between the monomer and polymer. Likewise, the epoxides cyclize to a considerable extent during cationic polymerization [1]. Thus, the product of the polymerization when ethylene oxide is used as a monomer is a mixture of linear polyether and cyclic oligomers, with relative proportions depending on the initiator and other reaction conditions. The cyclic oligomers are produced by a "back-biting" mechanism in which participates the oxygens of the polyether backbone and that can lead in some cases to the complete depolymerization of the polyether.

Homopolymerization of epoxides by cationic mechanism has been recently studied kinetically and by NMR spectroscopy [13] using methyltrifluorosulfonate as initiator. They conclude, that the propagation occurs via nucleophilic attack of the monomer on the macrooxonium ion propagating specie to produce a polyether, although the presence of cyclic oligomeric products has also been observed.

In addition of the mechanistic disadvantages, the main drawback of the Lewis acids in the commercial use is their water sensitivity that makes their handle and storage difficult. Lanthanide triflates offer the advantages of their stability towards the hydrolysis, that can be obtained from a commercial source and that they exhibits an unusual strong Lewis acid character, good stability at room temperature and high solubility in organic compounds [4]. Solubility of the curing agent in the epoxide is very desirable because heterogeneous dispersions are liable to settle out or agglomerate during storage. It is also useful to be able to form a solution containing both epoxide and curing agent for the manufacture of prepregs.

The physical and mechanical properties of a thermosetting resin mainly depend on the degree of cure. On the other hand, the processability of a thermoset depends on the rate and extent of polymerization under process conditions. Thus, the kinetic characterization of the reactive resin is not only important for a better understanding of structure–properties relationships, but in optimizing process conditions. Among a great number of experimental techniques relating to the investigation of thermosetting cure reactions, differential scanning calorimetry (DSC) has been used by a number of workers to study the kinetics and thermal characteristics.

DSC scans of DGEBA samples containing the required amounts of ytterbium, samarium, cerium, dysprosium, erbium and lanthanum triflates has been dynamically registered (see Fig. 1). The thermal data obtained in the experiments are shown in Table 1. Very little proportions (1 phr) of initiator lead to a complete crosslinking in all cases. Moreover, only slight differences can be found between the onset temperatures of the crosslinking exotherms as well as the maximum temperature of the exotherms for the different catalysts. In the table, T_g of the crosslinked DGEBA is also collected. Some of these materials do not show baseline inflections attributable to glass transition, due to the low C_p differences. This seems
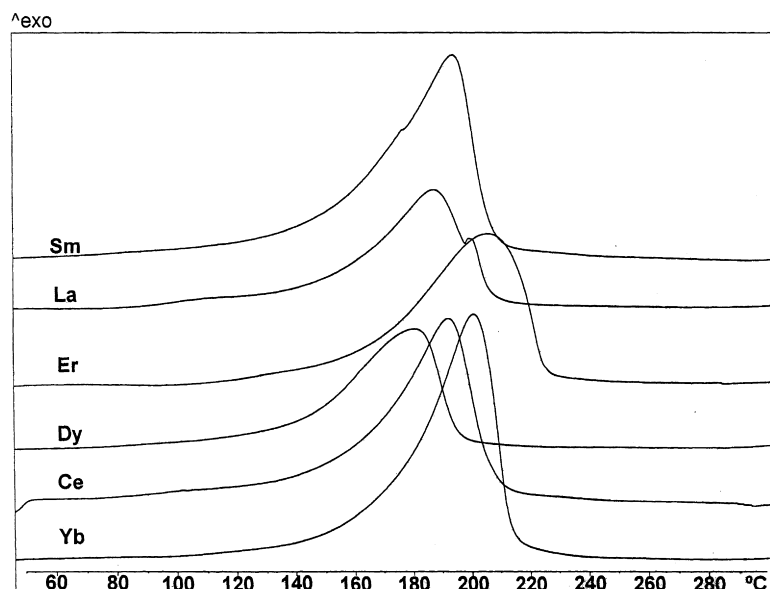
Fig. 1. DSC plots of DGEBA containing 1 phr of different lanthanide triflates as catalysts.

to support a high crosslinking density that immobilizes the polymer chain.

On comparing the values of crooslinking process with those obtained from the curing of a similar resin with a typical cationic initiator, $BF_3.MEA$ [14,15], it is noticeable that the crosslinking takes place at similar temperatures, although lower crosslinking enthalpy values were reported. Moreover, three exotherm peaks were observed on the DSC thermograms of $BF_3.MEA/DGEBA$ system. The first one was attributed to the coordination of the Lewis acid to the epoxide ring, the second, to the curing process and the third to an epoxy-OH reaction that takes place above 200°C, since $BF_3.MEA$ forms HBF_4 on heating. The exotherm due to the acid–base interaction was not observed in the case of the new catalyst. Thus, the enthalpy of coordination could be evolved during the process of sample preparation or could take place during the curing reaction, thus leading to unreliable crosslinking enthalpies. The absence in the new catalysts of a proton donor lead to the non-existence of the post-curing process.

Fig. 2 shows the dynamic DSC curves obtained from DGEBA and ytterbium triflate at different catalyst percentages. Table 2 shows the thermal parameters obtained from these experiments. As can be seen, there is a great dependence of the onset and maximum crosslinking exotherm temperatures on the proportion of catalyst. The higher the amount of the catalyst the lower the curing temperature. Surprisingly, as higher the amount of catalyst lower the curing enthalpy. A possible explanation can be found if we consider that side reactions take place in a higher extension when higher proportions of the catalyst are used.

Technologic application of epoxy resins needs the knowledge of time and temperature of processing to reach the complete cure of the material. Isoconversional kinetic analyses of non-isothermal data provide a useful tool to predict these application parameters. Isoconversional kinetic analysis is based on the idea that the reaction rate at a constant conversion depends only on the temperature.

As has been mentioned above, the use of Lewis acid initiators in the crosslinking of the epoxy resins can lead to back-biting or to chain transfer processes as parallel side reactions. Therefore, the application of kinetic analysis based on a single step kinetic equation can produce unreliable values of Arrhenius parameters for the whole process. Moreover, the resulting average values do not reflect changes in the reaction mechanism.

If changes in the mechanism are associated with changes in the activation energy, they can be detected by using the model-free isoconversional method [16]. This method is used to evaluate the E_a dependence for the curing and the interpretation of such dependencies is an useful application of this method [17]. For multi-step kinetics, the value of α, the extent of the conversion, determine the composition of the sample and the variation of E_a with this parameter reflects the relative contributions of single steps to the overall reaction rate [18]. To our knowledge, crosslinking of

Table 1
DSC data obtained from dynamic scans of DGEBA and 1 phr of different lanthanide triflates as catalyst (20°C/min)

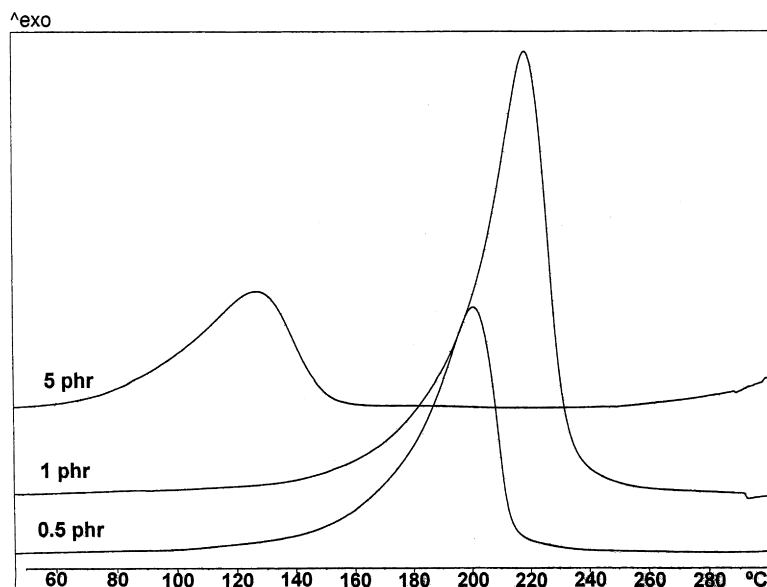| Catalyst 1 phr	T_{onset} (°C)	T_{max} (°C)	ΔH (KJ/mol)	T_g (°C)
$Yb(OTf)_3$	160	159	468	80
$La(OTf)_3$	149	187	473	–
$Ce(OTf)_4$	157	193	478	85
$Dy(OTf)_3$	134	180	475	79
$Sm(OTf)_3$	153	195	430	–
$Er(OTf)_3$	159	206	498	95

^exo

Fig. 2. DSC plots of DGEBA containing different amounts of ytterbium triflate as catalyst.

epoxy resins initiated by Lewis acid have not been studied by isoconversional analyses, therefore it is not possible to compare these initiators with the until now cationically available.

Fig. 3 shows the plots of E_a versus conversion degree at different initiator percentages. Curve corresponding to 0.5 phr of ytterbium triflate shows a straightforward line at conversions above 20%, indicating that there are not changes on the main process that takes place in this range. The E_a calculated for this proportion is about 80 kJ/mol slightly lower than the described for BF$_3$-MEA catalyzed.

Higher proportions of catalyst (5 phr) show a more complex pattern, that indicates that parallel side reactions such as back-biting or chain transfer processes could occur as is described for cationic processes [1].

This method lead to a great inaccuracy of the values obtained in the first part of the curve since the formation of the active initial species can lead to a variation of the E_a in the first steps of the reaction. Moreover, the change from kinetic to diffusion controlled curing at high conversions degrees lead to unreliable results at conversions higher than 80%.

Fig. 4 shows the plots of E_a versus conversion degree obtained from the different lanthanide initiators at a percentage of 1 phr. No significant differences can be found on the shape of this dependence for conversion degrees from 20 to 80% but different values of E_a are obtained. This value ranges from 60 to 90 kJ/mol, with the exception of the Er catalyst, which shows a much lower E_a (25 kJ/mol).

From these analyses the prediction of crosslinking degree from time and temperature of curing can be made [16,17]. Table 3 collects the predicted times necessary to reach a practically complete curing at different selected temperatures for ytterbium triflate at different proportions. As can

be seen, higher proportions of catalyst lead to shorter curing times thus allowing selecting the proper conditions for a technical application.

Table 4 shows the predicted heating times at different selected temperatures for the different lanthanide triflates at a percentage of 1 phr. As can be seen, Er catalyst shows the higher activity at lower temperatures and Sm catalyst is the most active at higher. As it was expected, all the catalysts show a very high reactivity at 200°C and need only few minutes to reach a complete cure. From a practical point of view, temperatures from 140 to 160°C are recommended with low catalyst proportions.

The values obtained from isoconversional kinetic analyses have been tested in order to prove their concordance with the experimental ones. So, isothermal scans were carried out at different selected temperatures and the time to reach a 95% of conversion was determined. As can be seen in Table 5, there is a good concordance between predicted and experimental values when the isothermal scans are carried out at temperatures in the range of the dynamic exotherm that varies for each catalyst, confirming the capacity of prediction of isoconversional analyses in this range. Predictions at lower temperatures lead to higher inaccuracy.

To determine the thermal stability of the materials obtained using the new catalysts, thermogravimetric

Table 2
DSC data obtained from dynamic scans of DGEBA and different amounts of ytterbium triflate as catalyst (20°C/min)

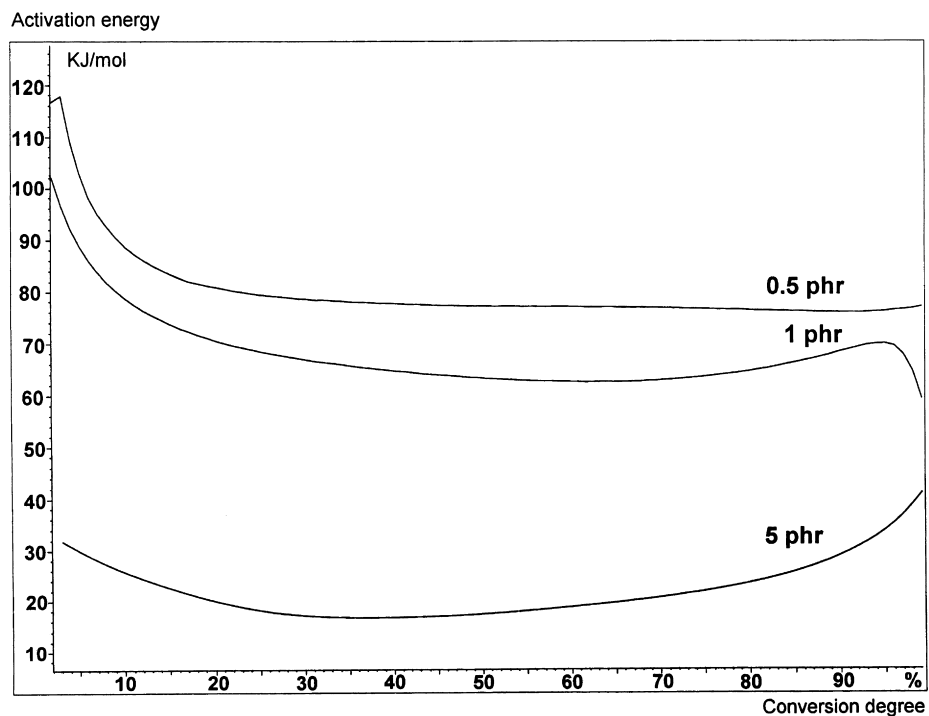| Catalyst	T_{onset} (°C)	T_{max} (°C)	ΔH (KJ/mol)	T_g (°C)
Yb(OTf)$_3$ 0.5 phr	170	203	518	79
Yb(OTf)$_3$ 1 phr	160	195	468	80
Yb(OTf)$_3$ 5 phr	82	126	441	–

Fig. 3. Plot of E_a vs. Conversion degree for the curing of DGEBA with different amounts of ytterbium triflate.
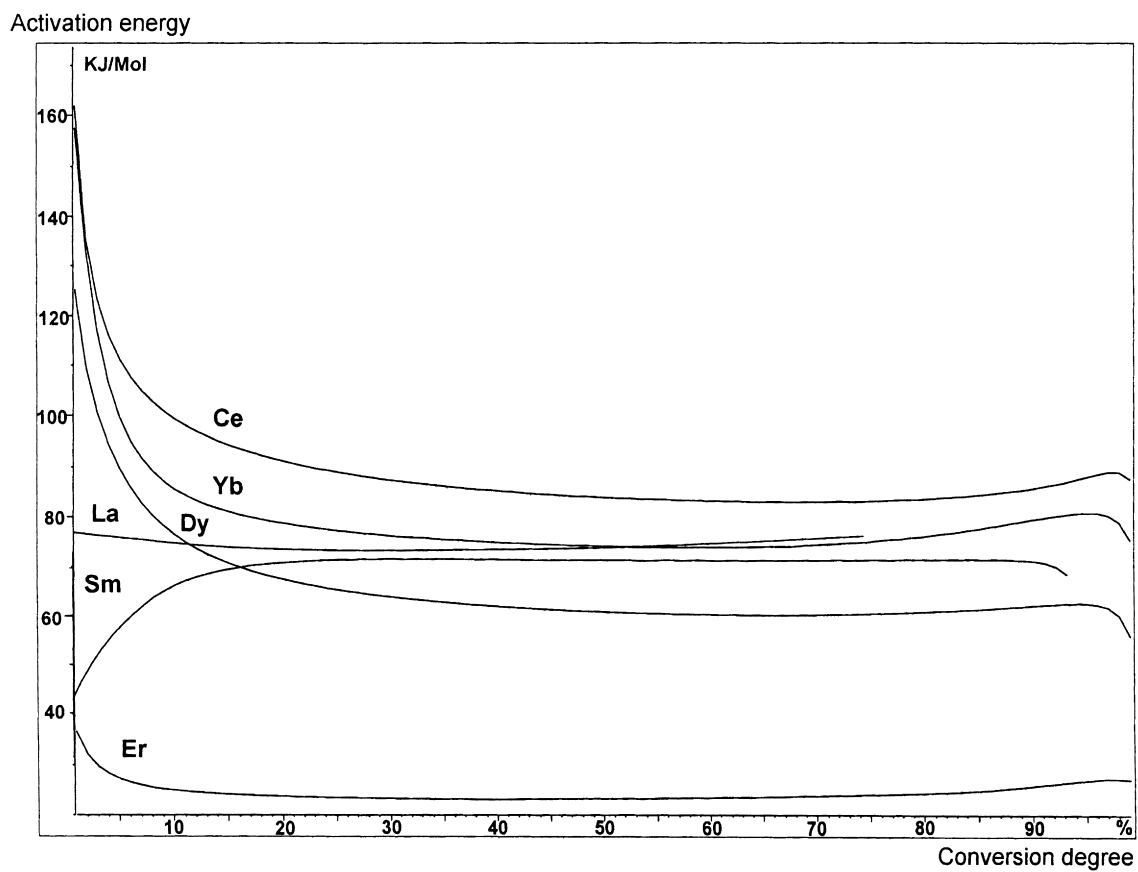

Fig. 4. Plot of E_a vs. Conversion degree for the curing of DGEBA with 1 phr of different lanthanide triflates.

Table 3
Predicted time (min) from isoconversional kinetic analysis to reach a conversion of 95% at different curing temperatures for DGEBA and different amounts of ytterbium triflate

Catalyst	140°C	160°C	180°C	200°C
Yb(OTf)$_3$ 0.5 phr	49	19	8	4
Yb(OTf)$_3$ 1 phr	49	17	6	2
Yb(OTf)$_3$ 5 phr	17	5	2	1

analyses were performed and the obtained thermal data are collected in Table 6. As can be seen, high thermal stability is achieved in all cases and there are not important differences depending on the nature and the proportion of the catalysts.

Dynamic mechanical analyses of the cured samples were carried out in order to test the mechanical properties of these materials and to obtain more information of the extent of curing and the morphology of the networks formed. The results of the dynamic mechanical studies are presented in Figs. 5–7. The drop in the storage modulus, and the corresponding maximum in the loss factor curves are due to the transitions associated with increases in internal freedom, such as long range segmental motions at the primary (α) transition and localized motions of chain segments or side-groups at the secondary (β) transition temperature.

In Figs. 5–7, the α- and the β-transition peaks are seen in the loss factor curves for all the samples studied. The α-transition peaks (Fig. 6) occur at 108.8, 95.1,124.8, 110.5 and 93.1°C for the samples of Yb, La, Ce, Dy and Sm, respectively. As is usual, the peak temperatures are higher than the T_g values determined by dynamic DSC studies due to a different definition of glass transition and the experimental differences in the transition from a glassy to a rubbery state. The β-transition peaks for all the samples occur over a broad temperature range of -100 to 0°C. The molecular origin of the β-transition in crosslinked epoxy resins has been associated with the sum of the motions of diphenyl propane groups and the hydroxy ether segments of the main chain [19]. This transition is also particularly sensitive to moisture content [20]. The partially reacted groups which result in ineffective crosslinks and dangling chains can also contribute to the broadness of α and β peaks [21]. In Fig. 6 the position and amplitude of the

Table 4
Predicted time (min) from isoconversional kinetic analysis to reach a conversion of 95% at different curing temperatures for DGEBA with 1 phr of catalyst

Catalyst	120	140	160	180	200
Yb(OTf)$_3$	–	49	17	6	2
La(OTf)$_3$	88	29	10	4	2
Ce(OTf)$_4$	–	54	17	6	2
Dy(OTf)$_3$	44	17	7	4	–
Sm(OTf)$_3$	44	15	6	2	1
Er(OTf)$_3$	29	20	14	10	7

Table 5
Predicted and measured times to reach a practically complete cure using DGEBA and 1 phr of lanthanide triflates

Catalyst		140°C	160°C	180°C	200°C
Yb(OTf)$_3$	Predicted	49	17	6	5
	Measured	35	16	5	4
La(OTf)$_3$	Predicted	29	11	4	2
	Measured	20	12	4	2
Ce(OTf)$_4$	Predicted	55	7	6	2
	Measured	52	13	6	4
Dy(OTf)$_3$	Predicted	18	8	5	1
	Measured	23	11	5	2
Sm(OTf)$_3$	Predicted	16	6	3	1
	Measured	19	7	4	1
Er(OTf)$_3$	Predicted	20	14	10	7
	Measured	22	17	9	7

α and β peaks show a different mobility of the networks formed for the different catalyst. In the frame inside of Fig. 7, the differences of the β relaxations between the 0.5% Yb and 1% Yb reflects the different degree of cure of these samples.

The temperature dependence of the glassy-state moduli of all samples is shown in Fig. 5. The modulus varies linearly with temperature in the first range and then the slope change over the β-transition interval. This change can be attributed to the freezing of the localized motions of the molecular groups responsible for the β-transition. Similar relations between molecular relaxations and macroscopic mechanical properties have been observed in impact and stress studies [22]. In Fig. 5 can be observed that the magnitude and temperature dependence of the moduli of the samples studied are not the same. The differences can be attributed to the different networks due to the side reactions, taking place in a different extend and to the template effect of the lanthanides but specially to the efficiency of each catalysts to achieve a high degree of cure. According to the DMTA results, the Ce samples achieve the highest curing degree and the Sm the lowest.

On comparing samples obtained with different catalyst percentage, 0.5 and 1% of Yb triflate, a higher degree of

Table 6
Thermogravimetric data of the cured samples of DGEBA with the different catalysts

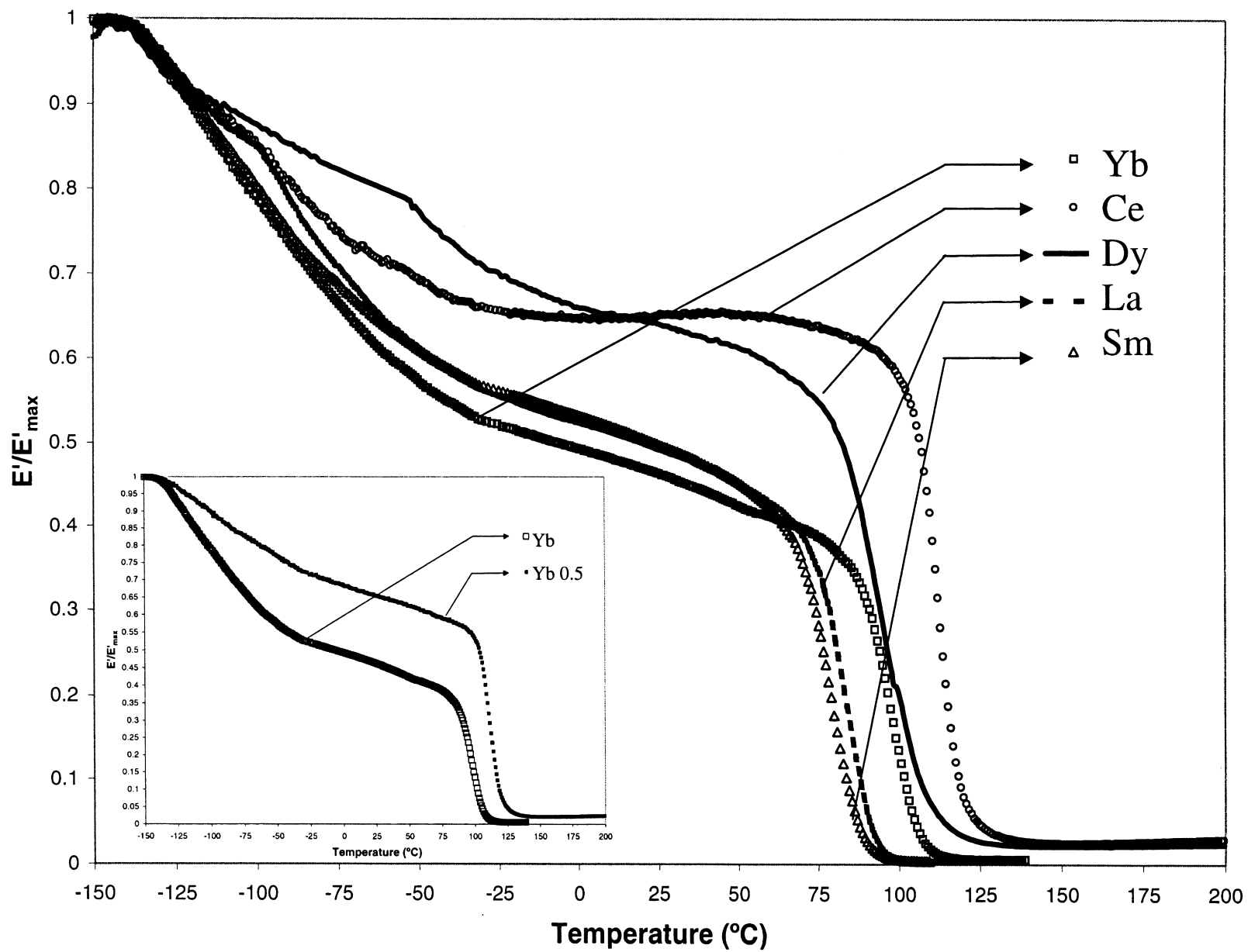| Catalyst 1 phr	T_{onset} (°C)	T_{max} (°C)	Char yield 600°C
Yb(OTf)$_3$[a]	331	370	16
Yb(OTf)$_3$	320	377	17
Yb(OTf)$_3$[b]	322	334	14
La(OTf)$_3$	339	382	14
Ce(OTf)$_4$	323	380	18
Dy(OTf)$_3$	339	370	16
Sm(OTf)$_3$	334	367	15
Er(OTf)$_3$	337	376	19

[a] 0.5 phr.
[b] 5 phr.

Fig. 5. Normalized storage modulus (E'/E'_{max}) as a function of temperature of the DGEBA and 1 phr of different lanthanide triflates. Frame inside: Comparison of the normalized storage modulus of two DGEBA samples cured with 1 and 0.5 phr of ytterbium triflate.
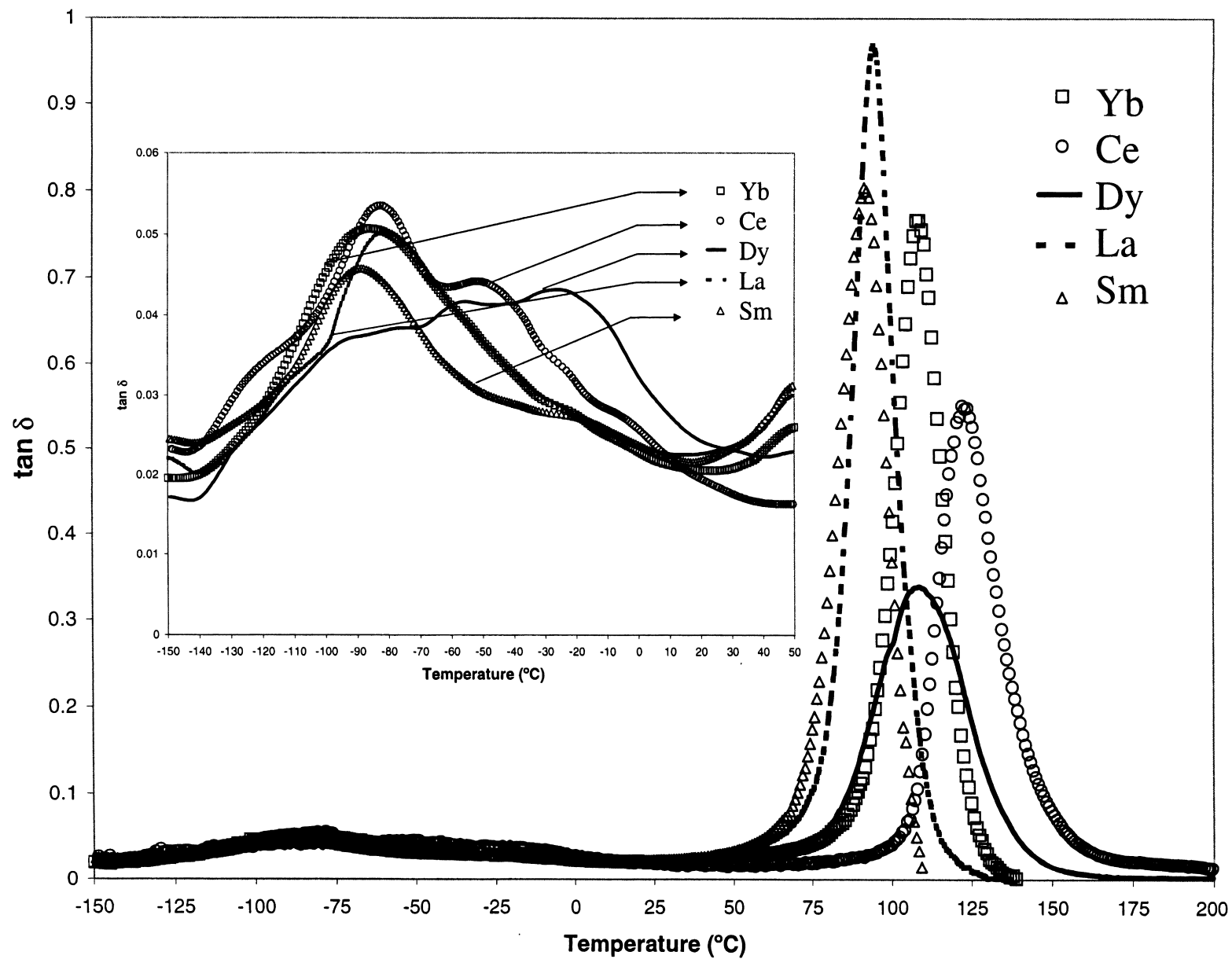
Fig. 6. Loss factor (tan δ) as a function of temperature of the DGEBA and 1 phr of different lanthanide triflates. Frame inside: expand of −150 to 50°C temperature range.
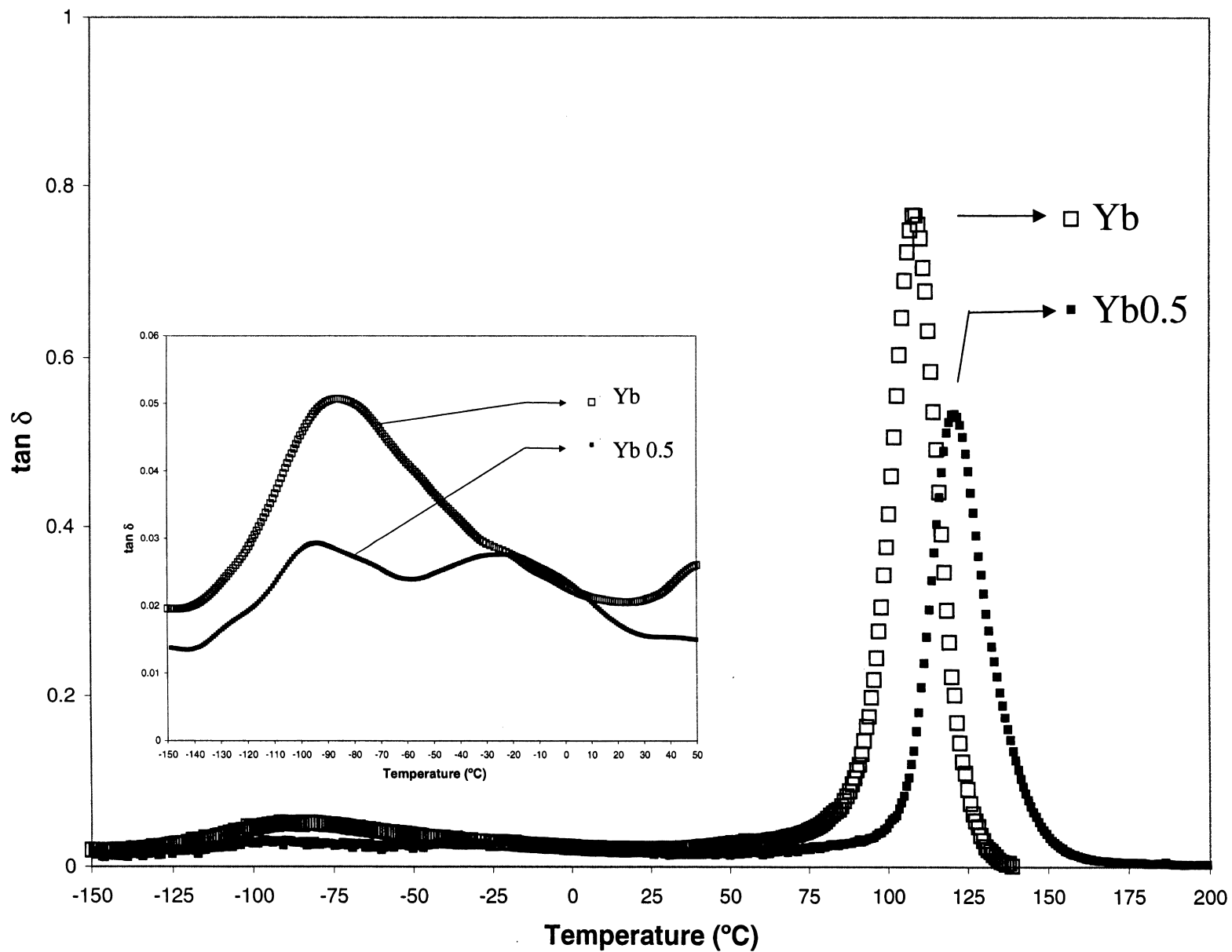
Fig. 7. Loss factor (tan δ) as a function of temperature of two DGEBA samples cured with 1 and 0.5 phr of ytterbium triflate. Frame inside: expand of -150 to 50°C temperature range.

curing is observed at lower proportions of the catalyst, thus confirming that higher proportions of the catalyst can lead to depolymerization processes. All these results are in a great concordance with the DSC conclusions previously discussed.

Thus, in the present work has been demonstrated the ability of lanthanide triflates, even in very little proportions, to crosslink epoxide resins at moderate temperature and their applicability in technology because of their stability even in the presence of moisture.

Acknowledgements

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