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New degradable thermosets obtained by cationic copolymerization of DGEBA with an s(γ-butyrolactone)

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Abstract

Diglycidylether of bisphenol A (DGEBA) was cured with different proportions of 1,6-dioxaspiro[4.4]nonane-2,7-dione (s(γ-BL)) with ytterbium triflate as initiator. The curing was studied with differential scanning calorimetry (DSC) and Fourier transform infrared in the attenuated total reflection mode (FTIR/ATR). FTIR/ATR was used to monitor the competitive reactive processes and to quantify the conversion of the epoxide, lactone and intermediate spiroorthoester (SOE) groups. The shrinkage undergone during curing was monitored by means of thermomechanical analysis (TMA). By combining the results obtained by FTIR/ATR and TMA, the processes that were and were not responsible for shrinkage were identified. The thermal and dynamic mechanical properties of the cured materials were determined by DSC and by dynamic mechanical thermal analysis (DMTA), respectively. The kinetic triplet associated with calorimetric curing was determined by means of isoconversional analysis. An increase in the proportion of lactone results in an increased curing rate, a decrease in shrinkage after gelation and a decrease in the glass transition temperature (T_g). Finally, as a preliminary measure, we examined the potential of the systems studied as reworkable materials by means of hydrolytic and thermal degradation. An increase in the ester units in the network results in materials that are less thermally stable and whose controlled degradability is greater.

Keywords: Epoxy networks; Lactones; Shrinkage

1. Introduction

In thermoset resins, shrinkage during the curing process may reduce their durability due to internal stress, the formation of microvoids, the loss of adherence on the substrate, etc. [1]. Ring-opening polymerization of heterocyclic monomers without the formation of small molecules as a by-product can lead to materials that shrink little or even expand [2,3]. Spiroorthoesters (SOEs) are bicyclic compounds that are commonly used to reduce shrinkage. Some SOEs can easily be synthesized from lactones and epoxides [4,5]. The copolymerization of epoxy monomers with lactones, with the intermediate formation of SOE that subsequently polymerizes, may be an appropriate procedure for reducing shrinkage during curing [6]. In previous works [7–9], diglycidyl ether of bisphenol A (DGEBA) or cycloaliphatic epoxy monomers were copolymerized with γ-butyrolactone (γ-BL) using various lanthanide triflates as initiators. The addition of small amounts of γ-BL made it possible to obtain materials with glass transition temperatures that are slightly below those of pure epoxy network and with low shrinkage after gelation, which allows internal stresses to be reduced. The use of a bicyclic lactone with a functionality of 4, rather than a single cycle lactone with a functionality of 2, makes it possible to obtain materials that are similar but which have a higher glass transition temperature, due to the formation of more points of crosslinking if the two lactone cycles polymerize.

The 1,6-dioxaspiro[4.4]nonane-2,7-dione, s(γ-BL), is an expandable monomer [1]; therefore, it could be used to reduce shrinkage during curing. The problem resides in the fact that the homopolymerization of five-membered lactones is a thermodynamically unfavourable process [3,10,11] that has only been observed in very extreme conditions [12,13]. Five- and six-membered lactones have been copolymerized by means of pseudoanionic catalysis using aluminium isopropoxide trimer or SmI_2/Sm as initiator, and can even form small

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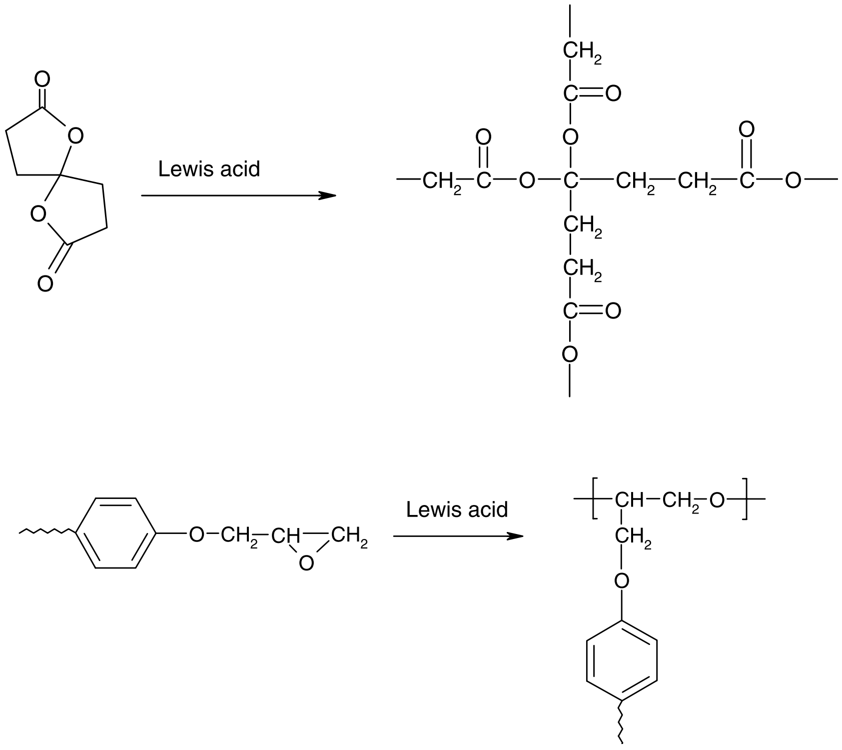
blocks of homopolymerized lactones [14,15]. The copolymerization of epoxy monomers with s(γ-BL) has been achieved by means of anionic catalysis [16–18], although it does not seem that lactone can homopolymerize in these conditions.

In a recent work [19], a cycloaliphatic epoxy monomer was copolymerized with s(γ-BL). It was seen that the use of a bicyclic lactone also reduces shrinkage after gelation and that part of the s(γ-BL) may even homopolymerize. The homopolymerization of the s(γ-BL), together with the polymerization of the SOEs formed, are reaction processes that reduce shrinkage. For this system, the following reaction processes have been shown to take place during curing: homopolymerization of the epoxy monomer and of the s(γ-BL), copolymerization of the epoxy monomer with s(γ-BL) to form mono-SOEs and bis-SOEs, copolymerization of the epoxy monomer with the mono-SOEs and bis-SOEs formed, and homopolymerization of the mono-SOEs and bis-SOEs. Schemes 1 (homopolymerization of monomers) and 2 (formation and polymerization of SOEs) show the reaction processes that are expected of the DGEBA/s(γ-BL) system studied in this work.

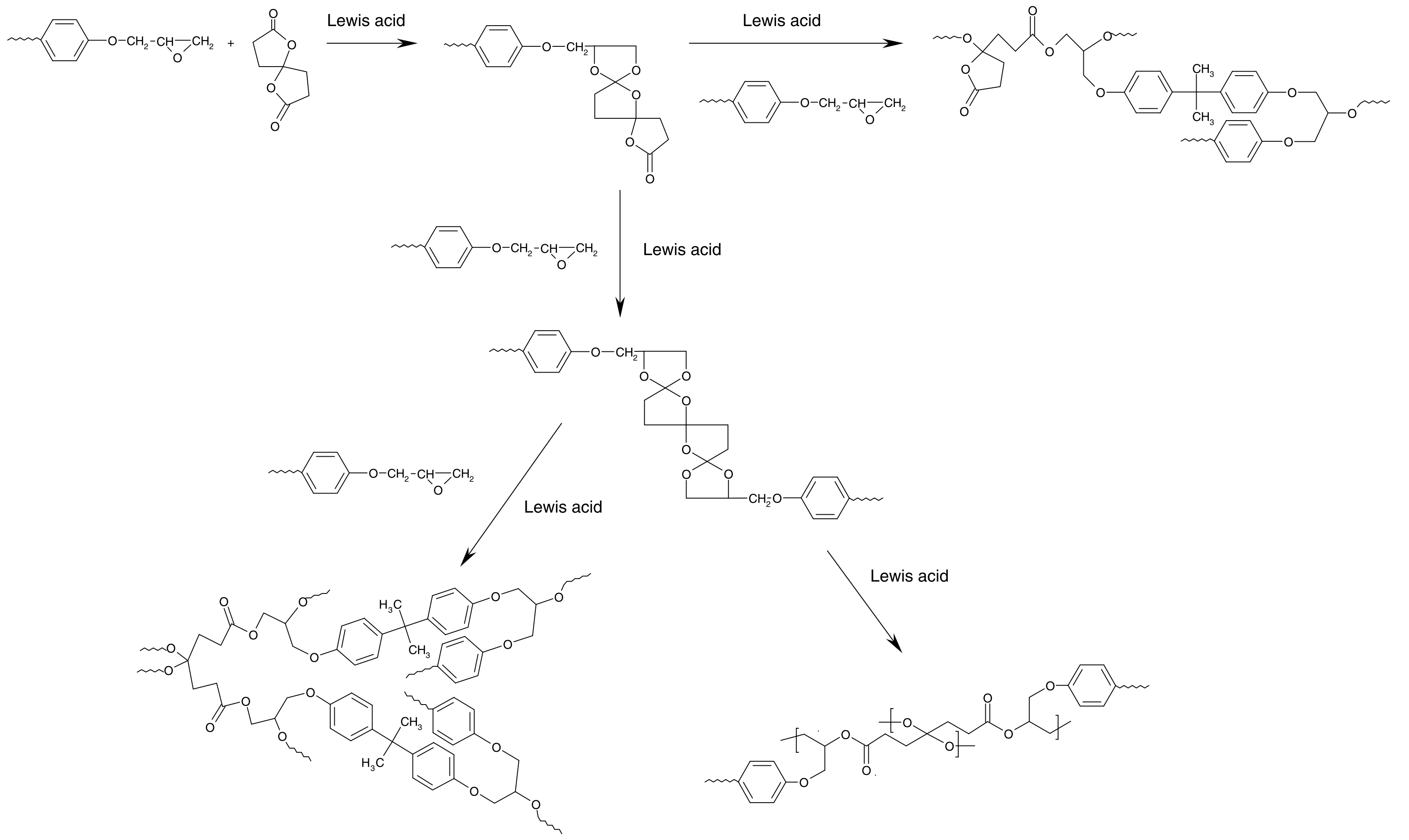
The high thermal stability and the insolubility of thermoset materials requires to produce materials with reworkable behaviour [20–24]. For certain applications, it is useful for these materials to lend themselves to controlled thermal or chemical degradation. For example, in electronic applications, a faulty processor could be replaced without the need to eliminate the whole of the printed circuit. The introduction of ester linkage in network structures can help to fulfil both of the aforementioned goals, as these linkages can be hydrolytically and thermally degraded. Furthermore, it should be possible to cleave these linkages easily under certain conditions but not during curing [20]. Several authors [21–23] have obtained thermally degradable thermosets from cycloaliphatic epoxies, which already contained ester units. These materials became more degradable when the primary carbon–ester linkages were replaced and turned into secondary or tertiary carbon–ester linkages. The problem with some reworkable cycloaliphatic epoxies, which are not thermally very stable, is that they degrade during the curing process. It is not usual to obtain reworkable epoxy networks from DGEBA, as it does not contain ester units and is not easily reworkable. Insert ester linkages into DGEBA-type networks may be a good strategy for bringing about a certain degree of degradability. Furthermore, the greater thermal stability of DGEBA suggests that the materials obtained do not degrade during the curing process. Recently, Wang et al. [24] obtained some reworkable cycloaliphatic resins with ether units that were free of ester groups.

As is shown in Schemes 1 and 2, the copolymerization of the DGEBA with s(γ-BL) allows the insertion of ester linkages, which may be primary, secondary or tertiary, depending on the predominant reaction processes. It is to be expected, therefore, that the materials obtained by means of this copolymerization will be potentially reworkable or at the very least more thermally degradable than the pure DGEBA.

In the present study, a DGEBA monomer with s(γ-BL) is copolymerized using ytterbium triflate as an initiator. The goal of the study is threefold: firstly, to examine the curing of the DGEBA/s(γ-BL) system and its properties; secondly, to compare the results obtained with those previously obtained using γ-BL; and finally, to make a preliminary study of the



Scheme 1. Homopolymerization of monomers (DGEBA and s(γ-BL)).



Scheme 2. Copolymerization of the DGEBA with s(γ-BL).

potential of the materials obtained as reworkable materials. The curing processes were monitored by means of DSC, FTIR and TMA and the dynamic mechanical properties by DMTA. The reworkable nature of the materials was studied using thermogravimetric analysis (TGA) and by means of hydrolysis tests in a basic medium.

2. Experimental

2.1. Materials

Diglycidylether of Bisphenol A (DGEBA) Epitoke Resin 828 from Shell Chemicals (epoxy equivalent = 187 g/equiv) was used as received. 1,6-Dioxaspiro [4.4] nonane-2,7-dione, s(γ-BL), (molecular mass = 156 g/mol, 98%) (Aldrich) and ytterbium (III) trifluoromethanesulfonate (99.99%) (Aldrich) were used as received.

2.2. Preparation of the curing mixtures

Samples were prepared by adding to the corresponding proportions of s(γ-BL) and DGEBA 1 phr of ytterbium triflate (1 part per 100 parts of mixture, w/w). DGEBA was kept for a while at room temperature and s(γ-BL) was crushed with a mortar. Samples were carefully stirred and kept at −20 °C before use to prevent polymerization.

2.3. DSC calorimetry

Calorimetric analyses were carried out on a Mettler DSC-821e calorimeter with a TSO801RO robotic arm. Samples of approximately 10 mg in weight were cured in aluminium pans in a nitrogen atmosphere. Non-isothermal experiments were performed between 0 and 225 °C at heating rates of 2, 5, 10, and 15 °C/min in order to determine the reaction heat. In the non-isothermal curing process the degree of conversion to a temperature T was calculated as the quotient between the heat released up to T and the total reaction heat associated with complete conversion of all reactive groups. The T_g of the cured materials was determined based on a second scan at 10 °C/min after dynamic curing.

2.4. FTIR/ATR spectroscopy

The isothermal curing process, at 150 °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. The disappearance of the absorbance peak at 915 cm^{-1} (epoxy bending) was used to monitor the epoxy conversion. The consumption of the reactive carbonyl group in s(γ-BL) was evaluated by measuring the changes in absorbance at 1795 cm^{-1} (carbonyl C=O stretching of cyclic ester). The appearance of the peak at 1740 cm^{-1} (carbonyl C=O stretching of aliphatic linear ester), which does not exist in the sample before curing, indicates that ring-opening polymerization has occurred in SOE. So, the latter was used to evaluate the SOE conversion. The peak at 1509 cm^{-1} (phenyl group) was chosen as an internal standard. Conversions of the different reactive groups, epoxide, s(γ-BL) and SOE, were determined by the Lambert–Beer law from the normalized changes of absorbance at 915, 1795, y 1740 cm^{-1}

$$\alpha_{\text{epoxy}} = 1-\left(\frac{\bar{A}^t_{915}}{\bar{A}^0_{915}}\right) \quad \alpha_{\gamma\text{-BL}} = 1-\left(\frac{\bar{A}^t_{1795}}{\bar{A}^0_{1795}}\right)$$
$$\alpha_{\text{SOE}} = \left(\frac{\bar{A}^t_{1740}}{\bar{A}^\infty_{1740}}\right) \tag{1}$$

where $\bar{A}^0$, $\bar{A}^t$ and $\bar{A}^\infty$ are the normalized absorbance of the reactive group before curing, after reaction time t and after complete curing, as we explained elsewhere [7–9,19].

2.5. Thermomechanical analysis (TMA)

The contraction undergone by the samples was studied using a Mettler TMA40 thermomechanical analyser. The samples were supported by two small circular ceramic plates and silanized glass fibres, which were impregnated with the sample.

Isothermal experiments at 150 °C was undertaken using TMA by application of a force of a 0.01 N in order to monitor contraction during the curing process. The degree of shrinkage α_{TMA} can be calculated as follows

$$\alpha_{\text{TMA}} = \frac{L_t - L_0}{L_\infty - L_0} \tag{2}$$

where L_t, L_0 and L_∞ represent, respectively, the thickness of the sample at time t, at the onset and at the end of the reaction.

Experimentally, one can determine the gelation point by using TMA starting at a region in which contraction is not observed between two contraction steps in the sample [7,8,25].

2.6. Dynamomechanical analysis (DMTA)

A DMTA Rheometrics PL-DMTA MKIII analyser was used. The samples were cured, before DMTA analysis, isothermally in a mould at 150 °C for 5 h and were then subjected to a post-curing at 180 °C for 4 h. Single cantilever bending at 1 Hz was performed at 2 °C/min, from −25 to 225 °C on prismatic rectangular samples ($1.5\times9\times5$ mm^3).

2.7. Measurement of density

The density of the samples was measured before curing at ambient temperature by directly measuring the sample using a pycnometer. For the cured samples, the density was determined indirectly by the flotation method, starting at dissolutions of KBr with densities lower and higher than that of the sample.

Table 1
Calorimetric data, densities, and shrinkage of the systems studied

Formulations[a]	Eq. initiator/ eq. epoxide	Eq. initiator/ eq. total	T_g (°C)	T_{max}[b] (°C)	Δh_{exp} (J/g)	Δh_{theo}[c] (J/g)	$\rho_{monomer}$ (g/cm^3)	$\rho_{polymer}$ (g/cm^3)	Shrinkage[d] (%)	Shrinkage[e] after gel. (%)
DGEBA/s(γ-BL) 1:0	0.0030	0.0030	133	178	563	563–563	1.167	1.193	2.20	0.79
DGEBA/s(γ-BL) 6:1	0.0032	0.0027	121	174	543	540–532	1.176	1.203	2.26	0.68
DGEBA/s(γ-BL) 4:1	0.0033	0.0026	113	170	534	529–519	1.177	1.208	2.55	0.65
DGEBA/s(γ-BL) 2:1	0.0036	0.0024	103	163	489	500–481	1.185	1.218	2.72	0.60
DGEBA/s(γ-BL) 1:1	0.0043	0.0021	78	154	459	456–423	1.204	1.240	2.93	0.31

[a] The composition of the formulation are given in molar ratios, and 1 phr of ytterbium triflate as initiator was used in all cases.
[b] Temperature of the maximum of the curing exotherm determined at a heating rate of 10 °C/min.
[c] Theoretical heat of polymerization determined using 105.3 kJ/equiv for epoxide and 15.4 kJ/equiv (first value) or 5 kJ/equiv (second value) for s(γ-BL).
[d] Total shrinkage determined as $(\rho_{polymer}-\rho_{monomer})/\rho_{polymer}$.
[e] Shrinkage after gelation determined using the total shrinkage and the α_{TMA} after gelation.

2.8. Kinetic analysis

Integral non-isothermal kinetic analysis combined with Coats–Redfern method [26] and/or with Criado's reduced master curves procedure [27] was used to determine the kinetic triplet [*A*, pre-exponential factor; *E*, activation energy; and $g(\alpha)$, integral function of degree of conversion]. Algebraic expressions for $g(\alpha)$ for the kinetic models used and details of the methodology used are explained elsewhere [25,28,29].

3. Results and discussion

3.1. Overall characterization

By means of calorimetry and density measurements, the materials were characterized before, during and after the curing process. Table 1 shows some of the results obtained. By increasing the amount of s(γ-BL), the experimental reaction enthalpy, Δh_{exp}, decreases, despite the increase in the total equivalents of reactive species. This is due to the fact that the polymerization enthalpy of lactones with five-membered rings is far less that of epoxy groups [10,11,30]. This fact may be related to the opening of a ring whose stress in the case of the epoxy group is greater than in the lactone. From the Δh_{exp} of the pure DGEBA a heat of 105.3 kJ/equiv was estimated. This value is similar to the reported [31] for other similar epoxy groups, and it was used, together with the theoretical heat for the γ-BL of 15.4 kJ/equiv [10] or 5 kJ/equiv [11], to determine the reaction heat, Δh_{theo}, associated with the complete conversion of all the reaction species. The similarity between the theoretical and experimental heat values (Table 1) makes it clear that both the epoxy groups and the s(γ-BL) units have reacted almost completely. This was proved by means of calorimetric tests and by FTIR of the materials that had previously been dynamically cured by DSC. No residual heat was observed by DSC and, by FTIR, the characteristic bands associated with epoxy and lactone groups were shown to have disappeared completely.

Table 1 shows that, by increasing the proportion of s(γ-BL), the T_g decreases due to the fact that the s(γ-BL) increases the flexibility of the network. If these results are compared to those previously obtained with γ-BL [7,8], for equivalent formulations, one can see that, with s(γ-BL), the T_g values obtained are significantly higher. As the s(γ-BL) has two lactone rings and the γ-BL only has one, equivalent formulations will be those that have half as many s(γ-BL) moles as γ-BL moles. As was expected, using s(γ-BL) with a functionality of 4 leads to materials that are more densely crosslinked than when a lactone with a functionality of 2 is used, such as the γ-BL.

By increasing the amount of s(γ-BL) a slight increase in total shrinkage is observed. Although this is not the desired effect, it should be taken into account that this shrinkage takes place in two stages, one before and one after gelation. The shrinkage after gelation is that which is not desired, as it takes place in a gel state, which causes internal stresses [3]. As will be seen below, an increase in the proportion of s(γ-BL) brings about the beneficial effect of a considerable decrease in the shrinkage after gelation. By comparing the use of s(γ-BL) with that of γ-BL [7,8] it can be seen that with the latter lactone shrinkage is generally slightly higher. This effect can be explained by the fact that when s(γ-BL) is used part of the lactone homopolymerizes instead of forming SOE. Whereas the formation of SOE is a process that is associated with a high degree of shrinkage [32], the ring-opening of this lactone is an expansion process, because of its expandable character. In the case of γ-BL there is no homopolymerization and almost all the lactone forms SOEs.

The effect of the composition on the curing kinetics was analyzed using DSC. Fig. 1 shows the conversion-temperature curves, α-T, which were determined by the integration of the calorimetric signal for the formulations studied. It can be seen that by increasing the proportion of s(γ-BL) the curing process is accelerated, resulting in curves α-T at lower temperatures. This effect, which has already been observed in other lactones and epoxy networks [7–9,19], might be apparently attributed to an increase in the proportion of initiator in relation to the epoxy groups (Table 1). In a previous study [7], it was seen that when ytterbium triflate was used as an initiator, it could coordinate both to epoxy groups and five-membered lactones. If this idea is taken to be true and if we take into account that the proportion of initiator in relation to all of the reaction groups decreases when the s(γ-BL) increases (Table 1), the acceleration effect detected should be attributed to the formation of more active initiator species due to the coordination of the initiator to the s(γ-BL). Some authors, using another cationic initiator, have observed and demonstrated the same type of behaviour [33–36].

Table 2 shows, for the various formulations studied, the kinetic parameters associated with dynamic curing by DSC, for a 0.5 conversion. For other conversions similar results have been obtained. The activation energies show a slight tendency to decrease when the proportion of s(γ-BL) increases. This trend is not very significant and does not clearly show the acceleration effect of the s(γ-BL), due to the compensation effect [25,29,37] between the activation energy and the pre-exponential factor. In order to show the effect of the s(γ-BL) on the curing kinetics more clearly, the rate constant, $k_{150\,^\circ\mathrm{C}}$, was calculated for a temperature of 150 °C. It can be seen that an increase in s(γ-BL) increases the rate constant, causing the curing reaction to accelerate. There is a direct linear relationship between the increase undergone by $\ln k$ and the proportion of s(γ-BL).

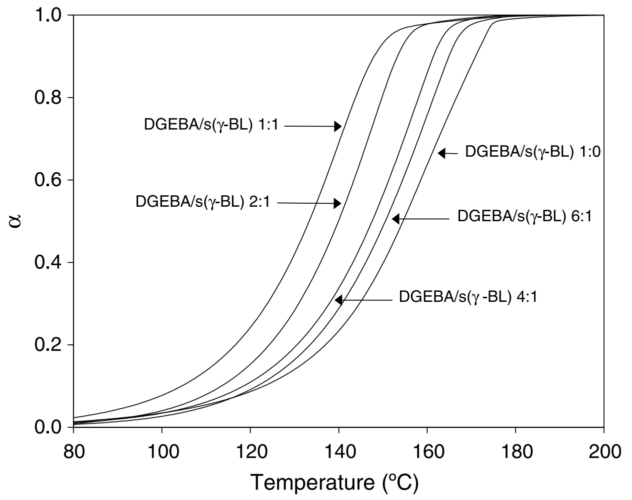


Fig. 1. Conversion degree versus temperature of non-isothermal curing for several DGEBA/s(γ-BL) formulations.

Table 2
Apparent activations energies, pre-exponential factors, and rate constants at a conversion of 0.5

Formulations[a]	E[b] (kJ/mol)	ln A[c] (s^{-1})	$k_{150\,^\circ\mathrm{C}}\times 10^{3}$[d] ($s^{-1}$)
DGEBA/s(γ-BL) 1:0	77.6	14.79	0.69
DGEBA/s(γ-BL) 6:1	79.2	15.51	0.90
DGEBA/s(γ-BL) 4:1	77.0	15.09	0.99
DGEBA/s(γ-BL) 2:1	73.9	14.48	1.44
DGEBA/s(γ-BL) 1:1	74.1	14.89	2.09

[a] The composition of the formulation are given in molar ratios, and 1 phr of ytterbium triflate as initiator was used in all cases.

[b] Values of activation energies were evaluated by isoconversional non-isothermal procedure.

[c] Values of pre-exponential factors for R_3 kinetic model with $g(\alpha)=[1-(1-\alpha)^{1/3}]$.

[d] Values of rate constant at 150 °C calculated using the Arrhenius equation.

In a previous study [8], for a formulation equivalent to DGEBA/s(γ-BL) 4:1, but using γ-BL, a value was obtained for $k_{150\,^\circ\mathrm{C}}$ that was practically the same as that obtained using s(γ-BL). This once again suggests that an increase in the reaction rate when the proportion of lactone increases should be attributed to the formation of more active initiator species and not to the viscosity of the medium, which would be much lower for the γ-BL.

3.2. FTIR characterization

To study the individual reactions that take place during the curing process and to establish the evolution of the different reaction groups, the curing of DGEBA/s(γ-BL) systems at 150 °C was followed by FTIR/ATR. Fig. 2 shows the spectra for the DGEBA/s(γ-BL) 4:1 formulation, including the changes that the most significant bands undergo, at different stages in the curing process. The reduction observed in the carbonyl bands at 1795 cm^{-1} of the s(γ-BL) indicates that SOE is formed. The appearance at 1740 cm^{-1} of a band of linear aliphatic ester groups in the polymer chain is associated with the ring-opening polymerization of the SOE. At high conversions, a 1720 cm^{-1} shoulder appears, which overlaps the 1740 cm^{-1} band. This shoulder also corresponds to linear carbonyls and is associated with the functional group's various chemical environments (Schemes 1 and 2). The great increase in the absorbance peak at 1100 cm^{-1} (C–O–C stretching of aliphatic linear ether), which was not used for calculations, reflects the build-up of the ether bond upon ring opening polymerization. The disappearance of the band at 915 cm^{-1} indicates that the epoxy group has polymerized. This band is overlapped by a 932 cm^{-1} band of the s(γ-BL) that also disappears during curing. To quantify the various functional

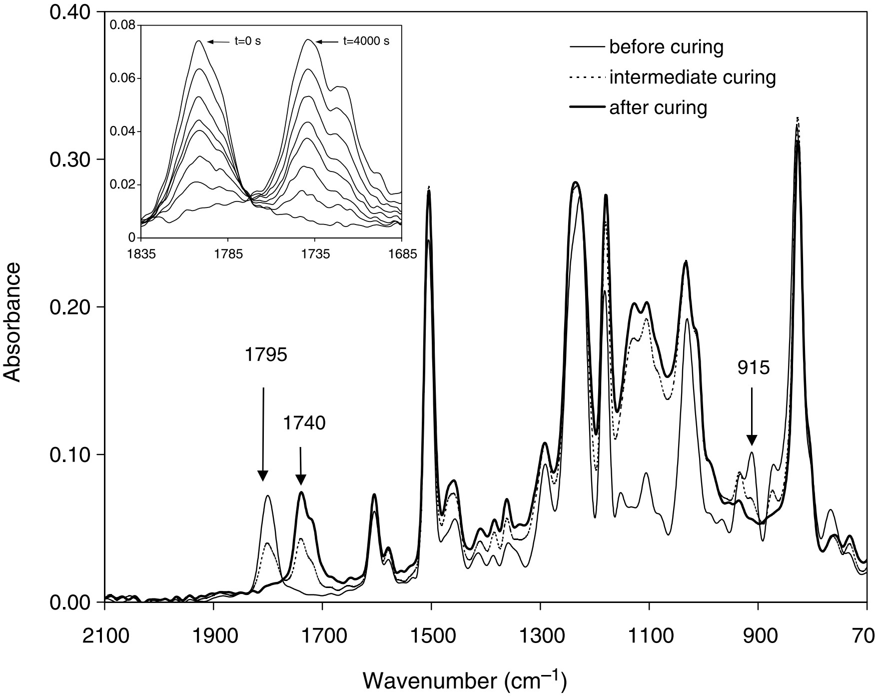


Fig. 2. FTIR spectra of the DGEBA/s(γ-BL) 4:1 formulation initiated with 1 phr ytterbium triflate at 150 °C before, intermediate and after curing. The inset shows the evolution of the carbonyl absorptions over time for the same formulation.

groups a deconvolution [7] of the overlapping bands at 1795–1740 cm^{-1} and at 915–932 cm^{-1} was necessary. For all of the formulations studied, a complete curing process took place, as the total disappearance of the s(γ-BL) and the epoxy groups showed. This result was confirmed by calorimetry: no residual heat was obtained for the samples previously cured by FTIR. Although the disappearance of the band at 1795 cm^{-1} is related to the formation of SOEs, when no epoxy groups are left it should be attributed to the homopolymerization of the s(γ-BL). Similarly, the increase of the band at 1740 cm^{-1} can also be attributed to lactone ring-opening during homopolymerization.

In a previous study, it was seen that DGEBA/SOE copolymerization is a more kinetically favourable process than the homopolymerization of SOE groups and that the latter process is only significant when the epoxy groups are exhausted [7]. In general, mono-SOEs are more likely to form than bis-SOEs, as the formation of bis-SOEs is more topologically inhibited and also requires the existence of mono-SOEs in order to take place. It is therefore assumed that the formation of significant quantities of bis-SOEs will take place when nearly all of the possible mono-SOEs have been formed. Fig. 3 shows the conversions of different reaction groups against time for 4:1 and 1:1 formulations. Although the almost continuous slope in the level of conversion-time curve (Fig. 3) does not suggest the existence of different reaction processes, the analysis of the relative evolution of α_{epoxy}, $\alpha_{\mathrm{s(\gamma\text{-}BL)}}$ and α_{SOE} indicates the existence of such processes. For a conventional 4:1 formulation, it can be seen that at the beginning of curing the epoxy groups and s(γ-BL) react almost simultaneously, indicating that the DGEBA/s(γ-BL) reaction for the formation of mono-SOEs and the homopolymerization of the epoxy groups are kinetically similar reactions. When s(γ-BL) approaches a 0.5 conversion, the formation of bis-SOEs begins, which takes place at a slower rate than the homopolymerization of the DGEBA. At longer curing times when no epoxy groups remain, no further SOEs are formed and the s(γ-BL) homopolymerizes. The polymerization of the SOEs takes place at a slower rate in relation to their formation. As long as there are epoxy groups, most of the SOEs copolymerize with the DGEBA, and the SOE groups only begin to homopolymerize after 600 s. For times beyond 600 s, as there is no epoxy, the α_{SOE} includes the homopolymerization of SOEs as well as of s(γ-BL), whereas $\alpha_{\mathrm{s(\gamma\text{-}BL)}}$ only

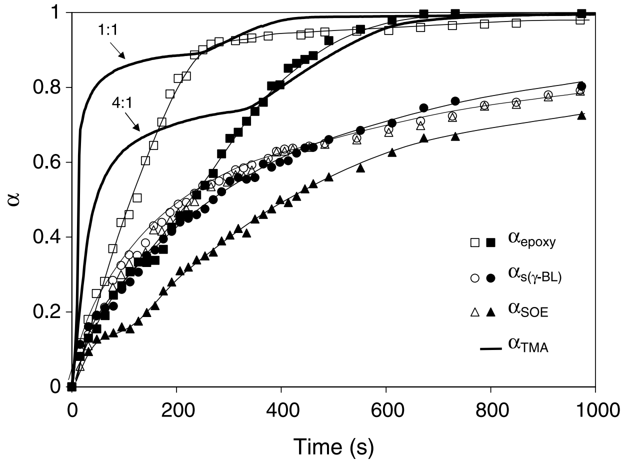


Fig. 3. Conversion of the various reactive groups (epoxy, s(γ-BL), and SOE) versus time for the DGEBA/s(γ-BL) 4:1 (filled symbols) and DGEBA/s(γ-BL) 1:1 (open symbols) formulations. Degree of shrinkage, α_{TMA}, versus time for the same formulations, indicated in the figure as 4:1 and 1:1. Isothermal experiments at 150 °C.

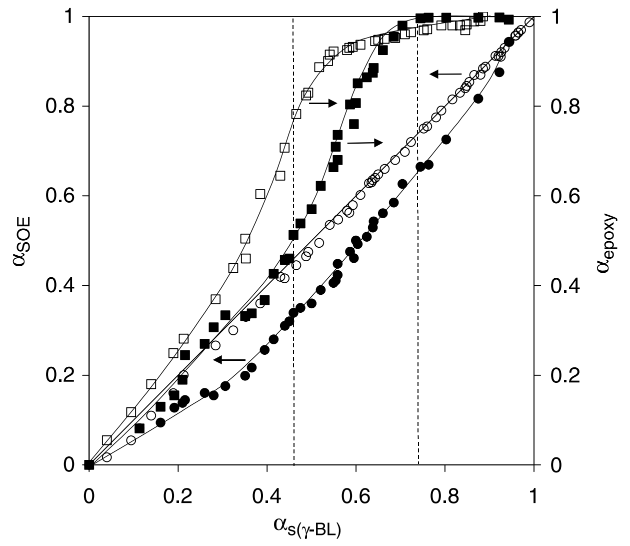


Fig. 4. Conversion of epoxy and SOE groups versus conversion of s(γ-BL) for the DGEBA/s(γ-BL) 4:1 (filled symbols) and DGEBA/s(γ-BL) 1:1 (open symbols) formulations. Isothermal experiments at 150 °C.

includes the homopolymerization of the s(γ-BL). Therefore, the difference between these two conversions will show the quantity of SOE that has homopolymerized.

In Fig. 4 the evolution of α_{epoxy} and α_{SOE} is plotted against $\alpha_{s(\gamma\text{-BL})}$ for several formulations. For the 4:1 formulation, the curing process, insofar as the elementary reactions are concerned, can be divided into three regions. In the first region up to $\alpha_{s(\gamma\text{-BL})}=0.5$ some epoxy groups react with the s(γ-BL) to form mono-SOEs. Most of the remaining epoxy groups homopolymerize and some of them copolymerize with the SOEs formed. In the second stage until the exhaustion of the epoxy groups, bis-SOEs are formed and homopolymerization of DGEBA and copolymerization of DGEBA/SOE takes place. In the last stage, in which there are no epoxy groups, approximately 25% of the s(γ-BL) and 10% of the SOEs homopolymerize. If one considers the results shown in Figs. 3 and 4 and the functionality of the reaction groups and their proportion in the mixtures one can deduce the proportions (percentage of equivalents) in which the different species react. In the 4:1 formulation, 67.5% of the DGEBA homopolymerizes, 17.5% copolymerizes with the s(γ-BL) and 15% copolymerizes with the SOE, while 75% of the s(γ-BL) copolymerizes with the DGEBA and the remaining 25% homopolymerizes. In terms of the SOEs formed, 90% copolymerize with the DGEBA and the rest homopolymerize.

In Figs. 3 and 4 the results for the 1:1 formulation are also shown. It can be seen that by increasing the proportion of s(γ-BL) all the reaction processes tend to accelerate. As $\alpha_{s(\gamma\text{-BL})}$ and α_{SOE} react during the whole of the curing process to the same degree, it can be said that the SOE groups react almost instantaneously when they form. These results once again show that the increased curing rate when s(γ-BL) is added must be attributed to the formation of more active species and not to the viscosity of the medium or the amount of initiator. It can also be observed that in the 1:1 formulation the epoxy groups are more rapidly exhausted. From this moment onwards no more SOE is formed, as large amounts of s(γ-BL) are homopolymerized in accordance with the existing formulation at the beginning of the curing process.

By comparing the results obtained by FTIR in the present study with those obtained with γ-BL in a previous study [7], it can be seen that the curing times are generally similar. The only differences observed are in the consumption of lactone and consequently in the consumption of SOEs. The γ-BL copolymerizes very quickly with the epoxy groups and it reacts throughout the curing process in the same proportion as the epoxy groups. However, when s(γ-BL) is used, this only occurs up to conversions close to 0.5. Thereafter, the s(γ-BL) reacts more slowly in relation to the epoxides, which may be due to the formation and homopolymerization of bi-SOE. The existence of a second ring in the s(γ-BL), which is not present in the γ-BL, must be the cause of the differences observed. It can therefore be concluded that the opening of the first ring in the s(γ-BL), for the formation of mono-SOEs, is kinetically equivalent to the DGEBA/γ-BL copolymerization. However, the opening of the second ring for the formation of bis-SOEs, and above all for homopolymerization, are more unfavourable processes, which take place at a slower rate. Another important difference is that the γ-BL never homopolymerizes and remains free without reacting when the epoxy groups are exhausted.

3.3. Contraction and gelation

Fig. 5 shows a plot of the degree of shrinkage, obtained by means of TMA at 150 °C, against the curing time for the various formulations studied. In every case shrinkage occurs in two stages, between which gelation takes place without any apparent shrinkage. By means of solubility tests in previous studies [7,8], the point of inflection in the shrinkage curve has been associated with gelation. For all the formulations studied, it was determined that the overall conversion in the point of inflection is close 0.6 and before this point the material is completely soluble in dichloromethane while after this point the solubility falls steeply. By increasing the proportion of s(γ-BL) gelation is reached earlier and at higher α_{TMA} values.

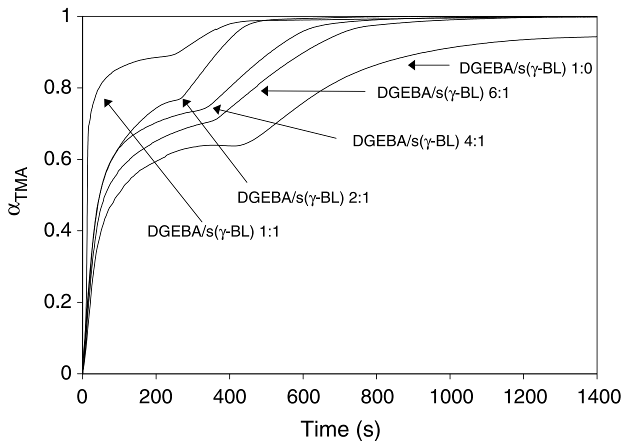


Fig. 5. Degree of shrinkage, α_{TMA}, versus the time for several formulations cured in a TMA instrument at 150 °C.

The shrinkage after gelation was calculated by taking α_{TMA} values and the total shrinkage during curing into account (Table 1). It can be observed that the formulations rich in s(γ-BL) shrink less after gelation and it is therefore expected that they will have less internal stresses.

In order to explain which elementary processes cause shrinkage and which do not, Fig. 3 shows the overlapping α_{TMA} versus time curves. For the DGEBA/s(γ-BL) 4:1 formulation, it can be observed that during the first stage of intense shrinkage ($\alpha_{\mathrm{TMA}} \approx 0.7$) the homopolymerization of the epoxy groups and the formation of SOEs are the main processes. In the second stage with less shrinkage ($\alpha_{\mathrm{TMA}} \approx 0.3$), the polymerization of the SOE and the homopolymerization of the s(γ-BL) are the main processes. The latter two processes, which can take place with almost zero shrinkage, are basically what cause the reduction in shrinkage after gelation. However, the formation of SOEs and the homopolymerization of the DGEBA are the source of the intense shrinkage prior to gelation. For the DGEBA/s(γ-BL) 1:1 formulation, the same behaviour is observed, but to a greater degree. After gelation there is almost no DGEBA left that can polymerize and the main reaction is the homopolymerization of the s(γ-BL). Due to this latter reaction, most of the curing process after gelation takes place without shrinkage.

3.4. Dynamic mechanical analysis

Figs. 6 and 7 show the mechanical relaxation spectra at 1 Hz of the different formulations studied. Table 3 contains the characteristic parameters associated with these spectra. Using a simplification of the simple rubber elasticity theory [38], one can estimate the network density with the following equation

$$M_{\mathrm{c}} = \frac{3\phi\rho RT}{E'_{\mathrm{r}}} \tag{3}$$

where M_{c} is the average molecular mass between crosslinkings; R is the gas constant; T is the absolute temperature in K, which takes a value of $T_{\mathrm{g}}+50$; E'_{r} is the relaxed modulus at this temperature; ρ is the density of the cured sample; and ϕ is the experimental front factor that takes a value of 1 for most polymers.

By increasing the proportion of s(γ-BL) in the samples, T_{g} (temperature of the maximum of the tan δ) and the modulus E'_{r} decrease due to the formation of more flexible structures in the cured material. It is possible that the lactone has a spacing effect between the DGEBA chains, which are more rigid, despite the fact that both components have the same functionality. The decrease observed in the T_{g} and in the E'_{r} can also be related to the dangling chains in the network, associated with the chain termination reactions, that exercise an internal plasticising effect.

The maximum of tan δ values obtained by DMTA follow the same trend as the calorimetric T_{g}, although the latter value is lower due to the lower equivalent frequency applied in the DSC [39].

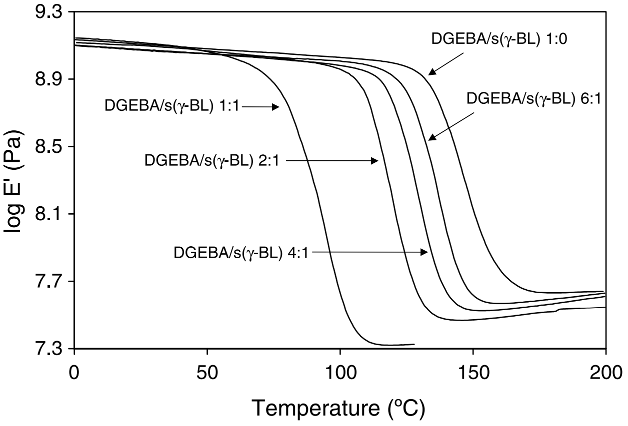


Fig. 6. Storage modules, log E', versus temperature at 1 Hz for several formulations DGEBA/s(γ-BL) studied.

From the data in Figs. 6 and 7, it is possible not only to determine the maximum tan δ value and E'_{r} but also the dispersity of the sample in terms of the amplitude of the tan δ peak or the decrease of E' when the material changes from a glassy to a rubbery state. In general, all the materials show a similar degree of dispersity and are fairly homogenous, as the transitions take place in a relatively narrow temperature range. The height of the peak of tan δ tends to increase slightly when the proportion of s(γ-BL) is increased, due to the greater mobility of the less crosslinked formulations when they undergo the glass transition.

Fig. 7 also includes the tan δ versus temperature curve for a sample with γ-BL whose composition is equivalent to that of the DGEBA/s(γ-BL) 4:1 formulation. Just as was seen by DSC, the glass transition appears at lower temperatures when the γ-BL was used, as the latter has a lower functionality than the s(γ-BL). The lower height value of tan δ when γ-BL was used must not be attributed to the density of crosslinking, which is less with γ-BL, but rather to the reaction processes that take place, which are slightly different for each lactone. A relaxation is also observed near room temperature that is due to the fact that part of the γ-BL has not polymerized.

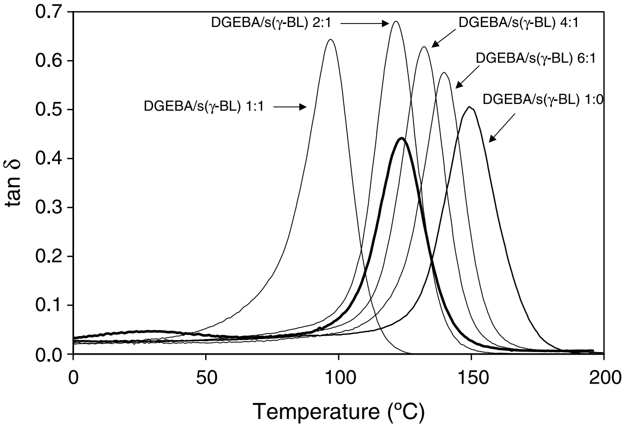


Fig. 7. tan δ versus temperature at 1 Hz for several formulations DGEBA/s(γ-BL) studied. The heavy lines represent the formulation with γ-BL, equivalent to DGEBA/s(γ-BL) 4:1.

Table 3
Results of the DMTA (1 Hz) and TGA analysis for the DGEBA/s(γ-BL) formulations studied

Formulations[a]	DMTA			TGA	
	$T_{\tan\delta}$[b] (°C)	E_r'[c] (MPa)	M_c	T_{onset}[d] (°C)	$T_{\max}$[e] (°C)
DGEBA/s(γ-BL) 1:0	149	41.6	338	268	346
DGEBA/s(γ-BL) 6:1	140	37.3	372	251	330
DGEBA/s(γ-BL) 4:1	132	35.5	386	245	325
DGEBA/s(γ-BL) 2:1	122	33.9	399	237	320
DGEBA/s(γ-BL) 1:1	97	26.8	485	220	306

[a] The composition of the formulation are given in molar ratios, and 1 phr of ytterbium triflate as initiator was used in all cases.

[b] Temperature of the maximum of the tan δ.

[c] Equilibrium storage modulus of material at the rubbery region at $T_{\tan\delta}+50$.

[d] Temperature of the onset decomposition based on the TGA data at 10 °C/min.

[e] Temperature of the maximum decomposition rate based on the TGA data at 10 °C/min.

3.5. Thermal and chemical degradation

As has been mentioned above, it may be useful to obtain thermosets that incorporate thermally labile groups whose decomposition can be controlled when they are heated at a certain temperature. By using thermogravimetric analysis and FTIR/ATR, the thermal decomposition of the DGEBA/s(γ-BL) mixtures was studied. In Table 3, it can be seen that mixtures with high amounts of s(γ-BL) decompose at lower temperatures. The ester groups are thermally weaker, and it is therefore logical that a greater number of ester groups makes the thermoset more reworkable. Despite this, all the polymers prepared do not decompose below 200 °C, which means that they do not degrade during the curing process.

It is known that the weaker tertiary ester linkages decompose at a lower temperature than secondary ones and these in turn at a lower temperature than primary ones [21,40]. When the s(γ-BL) homopolymerizes tertiary esters are formed, whereas the SOEs formed, when they open, only produce primary and secondary linear esters (Schemes 1 and 2). In order to try to prove the degradability, the DGEBA/s(γ-BL) 1:1 formulation was put at 250 °C and the mechanism was studied by FTIR. Fig. 8 shows the FTIR spectra before and after the degradation during 60 s, when no more changes can be observed in the FTIR spectrum. The intensity of the carbonyl band at 1740 cm^{-1} decreases slightly with thermal treatment and changes its shape. The formation of carboxylic acid could be confirmed by the appearance of a shoulder close to 1767 cm^{-1} and to the formation of a broad hydroxyl peak at 3450 cm^{-1}. The appearance of a weak peak at 901 cm^{-1} (C–H alkene) and the increase in the band at 1605 cm^{-1} (stretching C=C) could be indicative of the formation of alkenes [21,41]. All these results prove that the ester links break up to form carboxylic acids and alkenes, and that the process of thermal degradation occurs by a β-CH hydrogen transfer, according to the well-known thermal degradation mechanism of esters [41,42]. When other formulations with a lesser proportion of s(γ-BL) were tested, no signs of thermal degradation were detected by FTIR. This may be due to the lower proportion of ester groups and the fact that they are mostly secondary and primary.

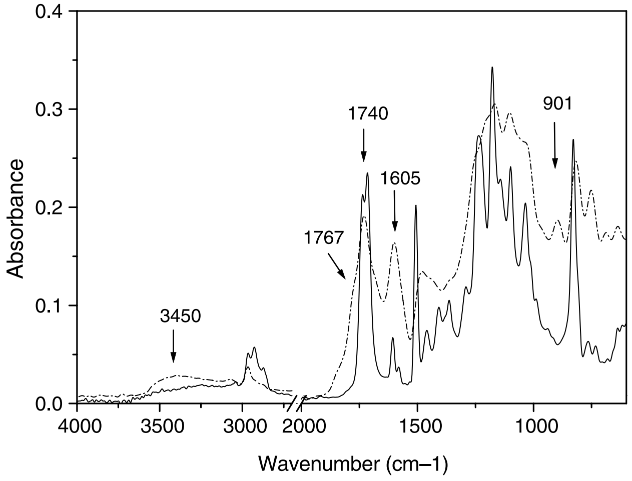


Fig. 8. FTIR spectrums of the DGEBA/s(γ-BL) 1:1 thermally degraded at 250 °C for 60 s (dash line) and no thermally degraded (solid line).

Finally, the materials prepared were hydrolyzed in a basic medium. In this case the degradation process was studied by means of solubility measurements and by FTIR/ATR. For all the formulations studied, after hydrolyzing at reflux ($T\approx 80$ °C) for 24 h in 1 M ethanolic KOH (ethanol/water 80/20 v/v), the ester band at 1740 cm^{-1} completely disappeared. During this process, an appreciable amount of soluble polymer (≈25%) was only detected in the DGEBA/s(γ-BL) 1:1 formulation. When there is a low proportion of ester groups, the long fragments generated during alkaline hydrolysis do not become soluble. When there is a greater proportion of s(γ-BL), the fragments generated are shorter and can become soluble.

4. Conclusions

The curing of DGEBA with s(γ-BL), initiated cationically with ytterbium triflate, makes it possible to obtain copolymers with a high proportion of ester groups, in which all the reaction species react completely. The homopolymerization of the s(γ-BL), when the epoxy groups are exhausted, explains why complete curing is attained.

The s(γ-BL) has an accelerative effect on the curing of the DGEBA due to the formation of more active species and not as a result of changes in the proportion of initiator or in the viscosity of the medium. This effect became apparent by means of FTIR/ATR and DSC experiments and through the kinetic parameters calculated. Due to the compensation effect between the activation energy and the pre-exponential factor, in order to compare the kinetic processes correctly it is necessary to determine the rate constant.

By increasing the proportion of s(γ-BL), more flexible copolymers with lower T_g are obtained. The s(γ-BL) produces materials that are more densely crosslinked and have a higher T_g value than the γ-BL, due to its greater functionality.

The addition of s(γ-BL) does not decrease overall shrinkage during the curing process. It does, however, reduce the shrinkage after gelation and consequently the internal stresses in the material.

The combined use of FTIR/ATR and TMA made it possible to identify the elemental reactions that are characteristic of DGEBA polymerization with s(γ-BL) and their relation to the shrinkage that takes place during the curing process. The ring-opening polymerization of the SOE groups formed and the homopolymerization of the s(γ-BL) are the reactions that are responsible for the reduction in the shrinkage after gelation and for the fact that part of the curing process during this stage take place without shrinkage. The shrinkage that occurs before gelation is due to the homopolymerization of the epoxy groups and the formation of SOE as a result of the reaction between the epoxy monomer and the s(γ-BL).

The insertion of ester groups, by means of the DGEBA/s(γ-BL) copolymerization, makes it possible to obtain thermosetting materials that can be degraded thermally or by alkaline hydrolysis in a controlled manner, but which are sufficiently stable not to degrade during the curing process.

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