Curing and Characterization of Oxazolidone-Isocyanurate-Ether Networks

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ABSTRACT: Oxazolidone-isocyanurate-ether networks were prepared by copolymerization of mixtures of DGEBA and toluene-2,4-diisocyanate (TDI) in presence of benzyldimethylamine (BDMA) as catalyst. Changes during curing and final properties of the cured materials were investigated by using DSC, FTIR/ATR, TMA, DMTA, TGA, and densitometry. The influence of the molar ratio of isocyanate to epoxide groups on the properties and curing were studied. The kinetics of curing was analyzed by means of an integral isoconversional nonisothermal procedure. The fractions of oxazolidone, isocyanurate, and ether groups present in the final network were evaluated and were found to be dependent on the initial isocyanate/epoxy ratio and curing conditions. By increasing the initial proportion of isocyanate the glass transition temperature, the thermal stability, the shrinkage, and the amount of isocyanurate rings increase, whereas the fraction of ether linkages and oxazolidones decreases. It was observed that the gelation is controlled by the formation of isocyanurate rings at the beginning of the curing. © 2012 Wiley Periodicals, Inc. J Appl Polym Sci 125: 2779–2789, 2012

Key words: epoxy resins; isocyanurate; oxazolidone; curing of polymers; networks

INTRODUCTION

Epoxy resins are a class of versatile thermosetting polymers widely used in structural adhesives, composites, and coatings in electrics and electronics. An important drawback, which limits some industrial applications, is that the cured materials are inherently brittle.[1] The addition of a tough second phase can offset this drawback but can cause a significant drop in heat resistance and glass transition temperature.[2–4]

Improving properties of epoxy resins at a lower cost is of a general great interest and can be used to make up for the decrease in certain properties when a second phase is added. A good strategy is to insert heterocyclic rings in the polymer structure, increasing the distance between crosslinks while increasing the rigidity of the structure. The reaction between diepoxides and diisocyanates can lead to thermosets containing isocyanurate and oxazolidone rings in their structure. Isocyanurates are crosslinking points, whereas oxazolidones are linear chain extenders that can improve the mechanical toughness of crosslinked isocyanurate containing networks. Both structures are well known for their high-thermal stability.[5] Although few studies report thermosets having these two kinds of heterocycles in the structure, it is accepted that these copolymers exhibit better properties than neat epoxy resins and other classical epoxy thermosets.[6–8] Consequently, the study of these systems has a remarkable interest.

A variety of catalysts has been claimed to be effective on the preparation of thermosets containing isocyanurate and oxazolidone rings. Among them, tertiary amines seem to be the most efficient and commonly used. The initiation mechanism catalyzed by tertiary amine has not been fully elucidated in bulk polymerization. Some authors proposed that two initiating species can be active in the anionic mechanism, a zwitterion formed by attack of the tertiary amine to the epoxide or a zwitterion formed by attack of the tertiary amine to the isocyanate.[9–11] The understanding of reactive processes implied in the curing can lead to an optimization of the network structure.

According to certain authors[5,6,8,9,12] the main reactions that take place, in order of increasing temperature, in epoxy/isocyanate/tertiary amine formulations are the following: (a) trimerization of isocyanate
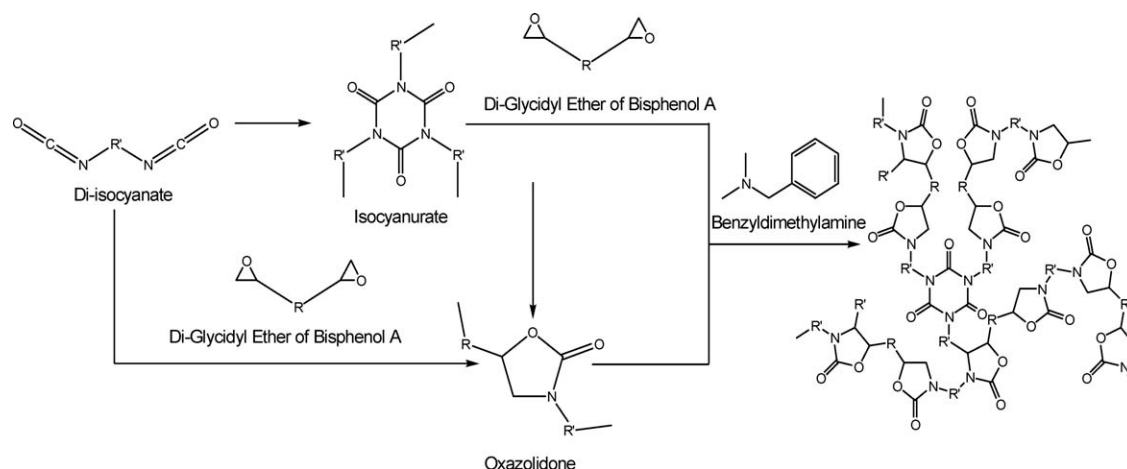
Scheme 1 Schematic reaction pathway for the formation of oxazolidone and isocyanurate structures.

(isocyanurate formation), (b) oxazolidone ring formation (epoxy-isocyanate reaction) and epoxy homopolymerization, and (c) isocyanurate decomposition to produce oxazolidone groups (isocyanurate-epoxy reaction). The fraction of oxazolidone, isocyanurate, and ether groups present in the final network depends on the initial isocyanate/epoxy ratio and curing conditions (curing temperature, kind, and amount of catalyst, etc). In general, homopolymerization of epoxide groups is considered as a secondary reaction. Scheme 1 depicts the reaction pathway expected in the formation of oxazolidone and isocyanurate structures.

In the present study, a low molecular weight DGEBA resin was cured with TDI using BDMA as the catalyst. The aim of our work is to study the influence of the molar ratio of isocyanate to epoxide groups on the curing and on the characteristics of the materials obtained.

We tested as catalysts three different tertiary amines: benzyldimethylamine (BDMA), 1-methylimidazole (1-MI), and 4-(N,N-dimethylamino) pyridine (DMAP), but BDMA was selected, since it was not able to homopolymerize neat DGEBA. This study was made to establish that the zwitterion formed between tertiary amine and isocyanate is the active species of initiator, which in addition could initiate the homopolymerization of DGEBA.

The different reactions that take place during the curing process were followed by FTIR and the fraction of oxazolidone, isocyanurate, and ether groups present in the final network were quantified by this technique. The properties of the materials were related with the final structure of the network, paying attention not only in the influence of the crosslinking density but also in the effect of the chain stiffness.

The kinetics of curing was studied by means of an isoconversional nonisothermal procedure that allowed us to determine the activation energy of the main reactive processes and reach some conclusions on the mechanism followed during curing.

Gelation was studied by means of nonisothermal TMA and DSC tests and the shrinkage during curing was determined by densitometric measurements. To the best of our knowledge, this is the first time that gelation and shrinkage have been determined for epoxy/isocyanate systems.

Thermal stability, glass transition temperatures, and dynamomechanical properties were investigated by means of TGA, DSC, and DMTA.

EXPERIMENTAL

Materials

Diglycidylether of bisphenol A (DGEBA), Epitoke Resin 828 from Hexion Specialty Chemicals (epoxy equivalent $= 187$ g eq^{-1}) was used after drying under vacuum. The 4-toluene-2,4-diisocyanate (TDI) from Aldrich was distilled. Benzyldimethylamine (BDMA), 1-methylimidazole (1MI), and 4-(N,N-dimethylamino)pyridine (DMAP) were purchased from Aldrich and used without further purification.

Preparation of the curing mixtures

Mixtures of TDI and DGEBA were carefully mixed with stirring and degassed under vacuum (at 80°C) during 2 h to prevent the appearance of bubbles during curing. Samples were kept at −20°C before use to prevent polymerization. About 1 phr of catalyst was added to the corresponding DGEBA/TDI mixtures at room temperature just before curing. Table I shows the notations and compositions of the different formulations studied. Thus, as an example, formulation notated as 2 : 1, contains 2 mol of DGEBA per 1 mol of TDI.

Formulation	n_{DGEBA} : n_{TDI}	eq_{BDMA}/eq_{TDI}	eq_{BDMA}/eq_{DGEBA}
DGEBA : TDI 2 : 1	2 : 1	0.03410	0.01705
DGEBA : TDI 1 : 1	1 : 1	0.02243	0.02243
DGEBA : TDI 1 : 2	1 : 2	0.01335	0.02671

Molar ratio is used as notation.

Calorimetric measurements

Calorimetric analyses were carried out on a Mettler DSC-822e calorimeter with a TSO801RO robotic arm. Samples of $\sim$ 10 mg in weight were cured in aluminium pans in a nitrogen atmosphere. Nonisothermal experiments were performed between 0 and 325°C at heating rates of 5, 7.5, 10, and 15°C min^{-1} to determine the reaction heat and the kinetics of curing. The degree of conversion, α, at a given 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 reaction rate, $d\alpha/dt$, was expressed as the ratio of the instant heat released (calorimetric signal) to the total reaction heat.

The glass transition temperatures of the fully cured materials ($T_{g\infty}$), after isothermal or dynamic curing, were determined in a heating experiment at 10°C min^{-1} as the temperature of the half-way point of the jump in the heat capacity when the material changed from the glassy to the rubbery state. The T_g of the uncured materials was determined in a heating experiment 10°C min^{-1} starting at -100°C.

Kinetic analysis

Kinetic parameters were determined using integral isoconversional nonisothermal kinetic analysis named Kissinger–Akahira–Sunose (KAS). For each conversion degree, the linear representation of $\ln(\beta/T^2)$ versus $1/T$ makes it possible to determine E and $\ln[AR/g(\alpha)E]$ from the slope and the intercept without knowing the kinetic model. β is the heating rate, T the temperature, E the activation energy, A the preexponential factor, R the gas constant, and $g(\alpha)$ the integral conversion function. Details of the kinetic methodology are given in a previous paper.[13] Although, the activation energy obtained by the integral procedure represents an average value up to a certain degree of conversion instead of the instantaneous and real value, it can be used for the discussion of the kinetics of curing.[14]

FTIR/ATR spectroscopy

Cured and uncured samples were analyzed with a FTIR spectrometer Bruker Vertex 70 with an attenu-ated total reflection accessory with thermal control and a diamond crystal (Golden Gate Heated Single Reflection Diamond ATR, Specac-Teknokroma). Spectra were collected at 30°C in the absorbance mode at a resolution of 4 cm^{-1} in the wavelength range of 600–4000 cm^{-1}. Ten scans were averaged for each spectrum.

The disappearance of the absorbance peaks at 915 cm^{-1} (epoxy bending) and 2260 cm^{-1} (carbonyl of isocyanate) indicates that the epoxide and isocyanate groups had reacted. The increase in the absorbance peak at 1100 cm^{-1} (C—O—C stretching of aliphatic linear ether) is related to the homopolymerization of epoxide groups. The appearance of absorption peaks at 1750 cm^{-1} (carbonyl of oxazolidone) and 1710 cm^{-1} (carbonyl of isocyanurate) shows the formation of oxazolidone and isocyanurate groups. Alternatively, the peak at 1410 cm^{-1} can be used to evaluate the formation of isocyanurate groups. The peak at 830 cm^{-1} (p-phenylene), which should not change during the curing process, was chosen as an internal standard.

Conversions of the different reactive groups, epoxide, isocyanate, isocyanurate, and oxazolidone, were determined by the Lambert–Beer law from the normalized changes of absorbance at 915, 2260, 1710, and 1750 cm^{-1}, respectively. Maximum normalized absorbances of isocyanurate and oxazolidone were determined in formulations where isocyanate groups were completely transformed into isocyanurate or oxazolidone groups. Maximum normalized absorbance of isocyanate and epoxy groups were determined from the initial spectrum of mixtures without initiator. The final composition (%) of oxazolidone, isocyanurate, and ether linkages was determined using FTIR conversion and the relative amounts of DGEBA and TDI present in the formulation. The homopolymerized DGEBA (ether linkages formed) was calculated as the difference between all the reacted epoxy groups and the groups that reacted to form oxazolidone rings.

Thermomechanical analysis (TMA)

Thermal mechanical analysis was carried out in a nitrogen atmosphere using a Mettler TMA40 thermomechanical analyzer. The samples were supported by two small circular ceramic plates and silanized glass fibres, which were impregnated with the sample. Nonisothermal experiments were performed between 30 and 325°C at heating rate of 5°C min^{-1} applying a periodic force that changed (cycle time = 12 s) from 0.0025 to 0.01 N. When the material reaches sufficient mechanical stability (gelation) the TMA measuring probe is not able to deform the sample and the amplitude of the oscillations is reduced. The gel point was taken in TMA as the
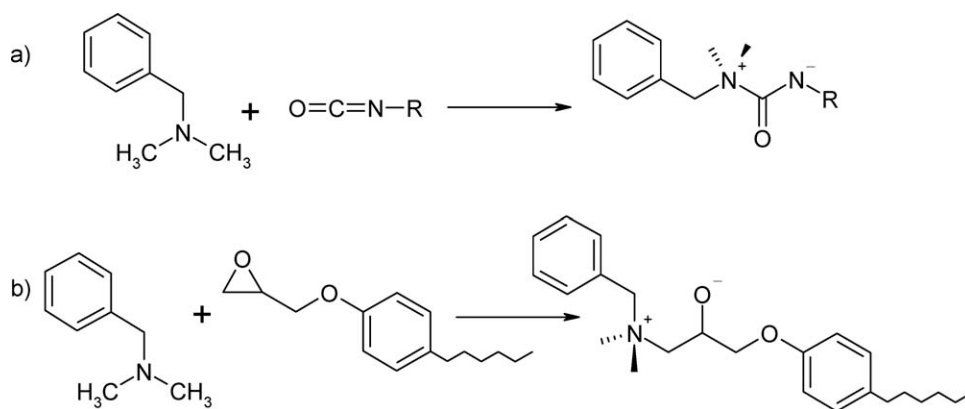
Scheme 2 Expected active initiating species formed (a) between BDMA and TDI and (b) between BDMA and DGEBA.

temperature at which a sudden decrease in the amplitude of oscillations was observed. The gel conversion, α_{gel}, was determined as the DSC conversion at $5°C$ min^{-1} at the temperature of the material gelled in TMA in a nonisothermal experiment. Details of the employed methodology are described in a previous work.[13]

Dynamomechanical analysis (DMTA)

DMTA was carried out with a TA Instruments DMA Q800. Single cantilever bending was performed on prismatic rectangular samples (ca. $0.5 \times 12 \times 25$ mm^3). The apparatus was operated dynamically, at $3°C$ min^{-1}, from -125 to $325°C$. The frequency of application of the force was 1 Hz and the amplitude of the deformation 30 μm. The samples used for the dynamomechanical analysis were cured isothermally by means of the following cure schedule: 1 h at $80°C$ plus 15 h at $200°C$ and finally subjected to a postcuring at $250°C$ for 1 h.

Thermogravimetric Analysis (TGA)

Thermogravimetric analysis was carried out in a nitrogen atmosphere with a Mettler-Toledo TGA-50 thermobalance. Samples cured following the above curing schedule, with an approximate mass of 5 mg, were degraded between 40 and $600°C$ at a heating rate of $10°C$ min^{-1} in a nitrogen atmosphere.

Measurement of density

The overall shrinkage was calculated from the densities of the materials before and after curing, which were determined using a Micromeritics AccuPyc 1330 Gas Pycnometer thermostatized at $30°C$. The shrinkage during curing was determined as:

$$\% \text{ shrinkage} = 100 \ \frac{\rho_\infty - \rho_0}{\rho_\infty}$$

where ρ_0 is the density of the uncured formulation and ρ_∞ is the density of the fully cured material obtained at the same conditions that DMTA samples.

RESULTS AND DISCUSSION

Initiation mechanism

First of all, we investigated the effect of three catalysts, the tertiary amines BDMA, DMAP, and 1MI, on the initiation mechanism and on the final properties and structure of the thermoset. According to the literature,[10] Scheme 2 show, as an example, the two active initiator species expected when BDMA is used as the catalyst in DGEBA : TDI formulations. We cured dynamically (between 0 and $325°C$ at $10°C$ min^{-1}) samples of DGEBA containing 1 phr of tertiary amine in the calorimeter. By nonisothermal DSC and FTIR of the samples cured in the DSC we proved that DMAP and 1MI can partially homopolymerize neat DGEBA whereas by using BDMA, no reaction was observed with DGEBA. However, Vazquez et al.[15] observed that this reaction took place using an appropriate amount of BDMA, at low temperature or employing low scanning rates in the DSC. When 5 phr of TDI was added to the formulations, neat DGEBA reacted completely with the three amines. These results suggest that DMAP and 1MI can form the two kinds of active species shown in Scheme 2. On the contrary, when BDMA is used, only the zwitterion formed between tertiary amine and isocyanate [Scheme 2(a)] becomes the true initiating species, whereas the zwitterion formed between tertiary amine and epoxide [Scheme 2(b)] is not active enough to homopolymerize DGEBA under the curing conditions used in this work. To go further in the formation of the active species of Scheme 2(b), we kept at $180°C$ for 2 h stoichiometric proportions of BDMA and phenylglycidylether (PGE) and then we registered the ^1H and ^{13}C NMR spectra. This way we proved that BDMA is unable to form

TABLE II
Final Composition and Temperature of Glass Transition for the 1 : 1 DGEBA : TDI
Formulations Cured Dynamically with 1 phr of Different Amines

Initiator	Oxazolidone[a] (%)	Isocyanurate[a] (%)	Ether[a] (%)	T_g (°C)
BDMA	20 (33)	40 (67)	40 (67)	189
1MI	42 (59)	29 (41)	29 (41)	181
DMAP	84 (91)	8 (9)	8 (9)	164

[a] % of oxazolidone, isocyanurate, and ether linkages in the final network. In brackets % of oxazolidone, isocyanurate, and ether formed with respect to the initial isocyanate or epoxy content.

an active species with the epoxy and that it is only able to produce the zwitterion by reacting with isocyanate, which is the active species responsible for the curing.

The DGEBA/TDI 1 : 1 stoichiometric formulations with 1 phr of BDMA, DMAP, or 1MI were investigated by DSC. After nonisothermal curing, the FTIR spectra of the thermosets showed that isocyanate and epoxide groups had disappeared completely, indicating that the materials obtained were fully cured. Table II summarizes the results obtained. It can be seen that DMAP promotes the formation of oxazolidone, whereas BDMA favors the formation of isocyanurate rings. Moreover, the glass transition temperature increases when isocyanurate content increases, as it is expected. These results suggest that changing the catalyst it is possible to tune the final properties of the thermosets and to obtain tailor-made materials with the desired properties. In this work, we selected BDMA as initiator because of the higher glass transition temperature achieved. In

addition, BDMA is the only amine that cannot initiate the epoxide homopolymerization reaction.

Curing mechanism

Samples with different DGEBA : TDI ratio were dynamically cured at 10°C min^{-1} with 1 phr of BDMA in the DSC and then the composition was determined by FTIR. Figure 1 shows the thermograms of the formulations studied. Three main exothermic peaks, which vary with the formulation, appear in the thermogram, at $\sim$ 45, 150, and 230°C. Moreover, the first peak has a shoulder close to 90°C. To determine the reactions involved, FTIR spectra of partially cured samples in the DSC up to several temperatures (i.e., 70, 130, 190, and 325°C for 1 : 1 formulation) after each exothermic peak or shoulder were recorded. The resulting spectra are shown in Figure 2 for 1 : 1 formulation. The final compositions and the evolution during curing, for all formulations, are collected in Table III.

The main reaction that takes place in the first exothermic peak (including the shoulder, until 110–
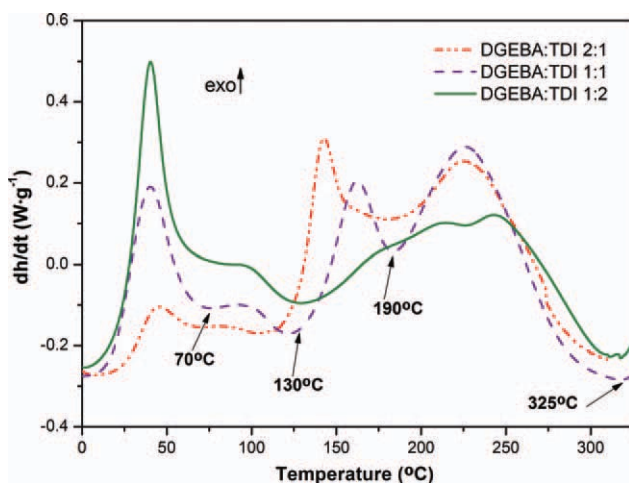
Figure 1 DSC thermograms of various DGEBA : TDI formulations cured with 1 phr of BDMA. Temperatures at FTIR spectra were recorded are indicated, as an example, for formulation DGEBA : TDI 1 : 1. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
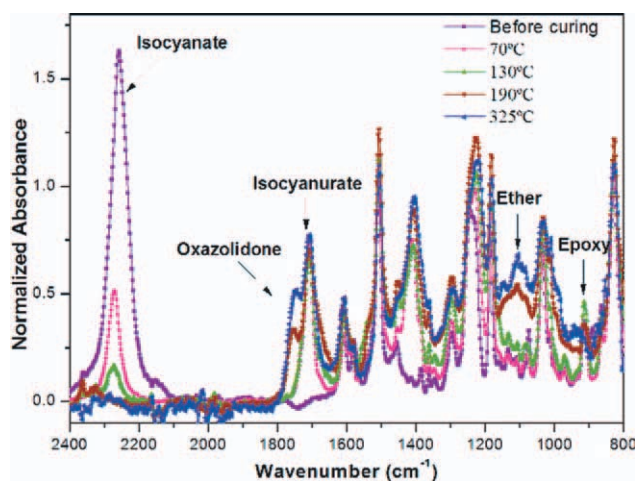
Figure 2 Evolution of the FTIR spectra of the DGEBA : TDI 1 : 1 formulations with 1 phr of BDMA during the DSC curing. FTIR spectrum before curing is included as reference. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

TABLE III
Evolution of the Content of Different Groups During Nonisothermal Curing up to Different Temperatures Indicated
in the Table Determined by FTIR Spectroscopy

Formulation	T (°C)	Isocyanate[a] (%)	Epoxy[a] (%)	Oxazolidone[b] (%)	Isocyanurate[b] (%)	Ether[b] (%)
DGEBA : TDI 2 : 1	70	17	100	0	83	0
	110	7	100	0	93	0
	170	0	87	14	86	6
	310	0	0	88	12	56
DGEBA : TDI 1 : 1	70	20	100	0	80	0
	130	9	100	0	91	0
	190	0	44	12	88	44
	325	0	0	33	67	67
DGEBA : TDI 1 : 2	80	34	100	0	66	0
	130	24	100	0	76	0
	190	13	70	3	84	24
	325	0	0	18	82	64

1 phr of BDMA was used as catalyst in all formulations.
[a] % of unreacted isocyanate and epoxide.
[b] % of oxazolidone, isocyanurate, and ether (epoxy homopolymerized) groups formed with respect to the initial isocyanate or epoxy content.

130°C) is the formation of isocyanurate rings. This reaction proceeds close to completion except for formulation with excess of isocyanate, where the conversion of isocyanate is about 75%. The formation of oxazolidone and the reaction of epoxide groups do not take place in this range of temperatures. The presence of two DSC peaks for the formation of isocyanurate rings has been observed by several workers[6,10] and can be related with the different reactivity of the two isocyanate groups of TDI or with the existence of noncatalyzed isocyanate trimerization giving isocyanurate rings at higher temperatures (shoulder about 90°C).

The second exotherm (between 130 and 190°C) is related to the formation of oxazolidone rings by reaction between isocyanate and epoxy groups, since the amount of oxazolidones increases whereas the amount isocyanurates barely decreases or even increases. Moreover, it is interesting to note that epoxy homopolymerization is another important reaction that competes with oxazolidone formation in this range of temperatures.

The main process taking place in the last exothermic peak is the decomposition of isocyanurate rings by reacting with the epoxy excess to give oxazolidone rings. This reaction occurs in greater extension in DGEBA-rich formulation (i.e., DGEBA : TDI 2 : 1) leading to networks with a higher amount of oxazolidone rings. On the contrary, in the formulation with the lowest proportion of DGEBA (i.e., DGEBA : TDI 1 : 2) the decomposition of isocyanurate rings is a secondary reaction and the network formed contains higher proportions of isocyanurate rings. DGEBA thermal homopolymerization is also an important reaction in this range of temperatures.

Scheme 3 collects the reaction mechanisms leading to the formation of isocyanurates (a) and oxazolidone rings (b). It can be observed as the zwitterion formed between tertiary amine and isocyanate acts as the initiating species in isocyanate trimerization and in the formation of oxazolidone rings.

Although, observing the FTIR spectra, it is possible to assign one or two main reactions to each exothermic peak; this assignment is only approximated since these peaks are partially overlapped. The exact composition of the network formed, and consequently the reactions that take place during curing, should be quantified (as shown Tables II and III). The initial composition of the formulation, the curing schedule and the catalyst used are the key parameters that control the composition of the resulting network.

Kinetics of curing

The mixtures of DGEBA : TDI were cured at several heating rates in the DSC. Table IV shows the experimental and theoretical heats of curing. Experimental heat, Δh_{exp}, was calculated as the average heat of the experiments at different heating rates and used to evaluate the degree of conversion. By increasing the proportion of TDI, Δh_{exp} increases, due to the different reaction heats of the reactive processes and to the different compositions. Δh_{theo} was estimated using the final composition (Table III) and the reported heats for isocyanurate (207.9 kJ mol^{-1}) and oxazolidone (179.5 kJ mol^{-1}) formation and for epoxy homopolymerization (80 kJ mol^{-1}).[16,17] The similarity between the theoretical and experimental values indicates that both the isocyanate and epoxy
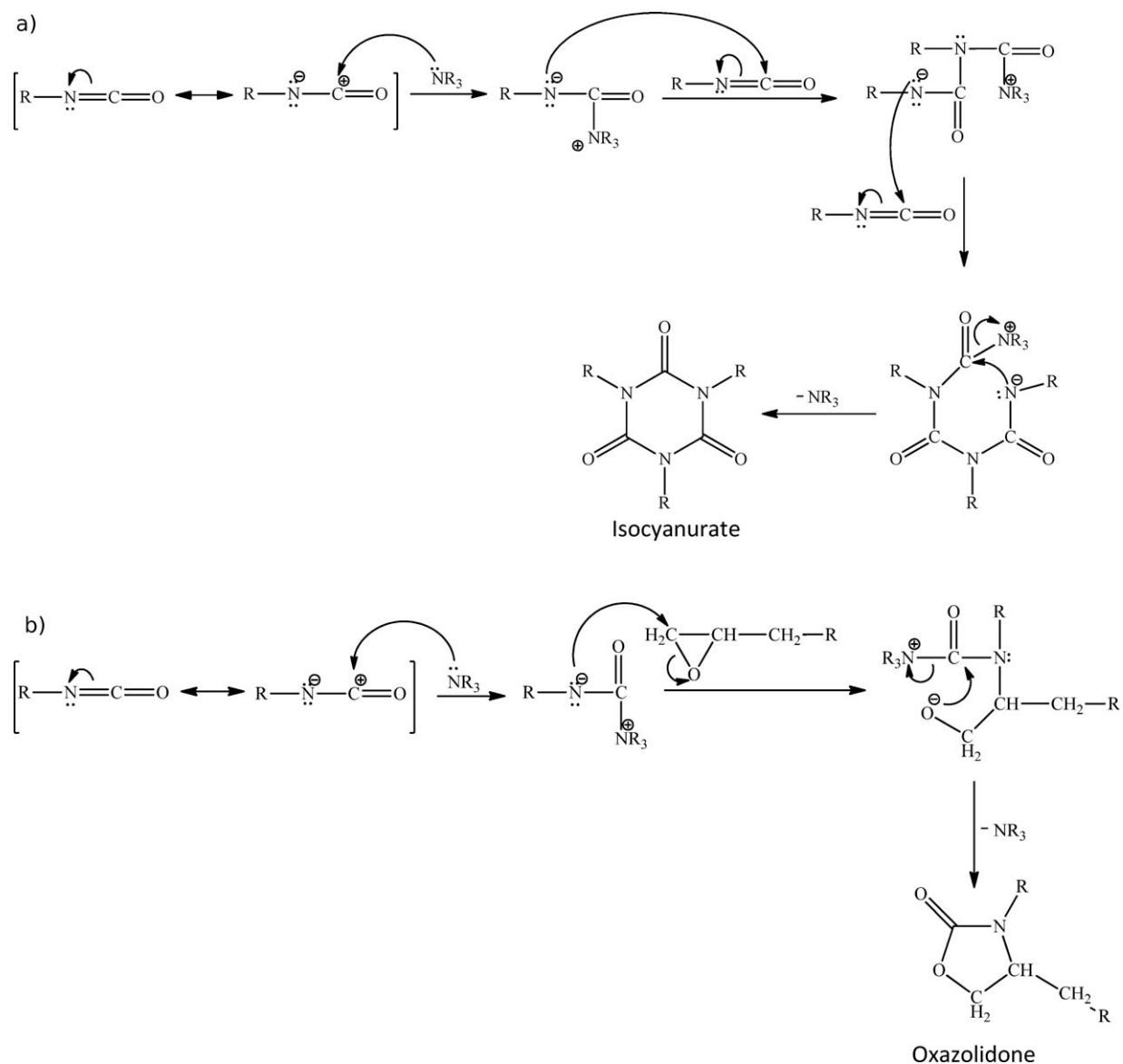
Scheme 3 Mechanisms of (a) isocyanate trimerization (isocyanurate formation) and (b) oxazolidone formation.

groups reacted completely, as we confirmed by FTIR, and that DSC is capable of recording all the heat of polymerization. Consequently, the calculated conversions (absolute conversions) (Table V) are correct and can be used in the kinetic analysis.

Because of the complexity of the curing process the kinetics was studied by the nonisothermal integral isoconversional procedure, because it is possible to determine useful information such as the apparent activation energy for every conversion without needing to know the kinetic model beforehand, which can change during the curing process. Table V summarizes the results obtained for the different formulations studied. The high regression coefficients r obtained indicate that the methodology is suitable for describing the kinetics of curing of these complex systems. In general, the activation energy is

lower during the first stages of the curing process and then increases slightly when the processes with greater activation energy initiate. Because of the compensation effect,[18] it is not possible to compare the activation energy values of the different formulations, but their changes during curing can be related with the different reactive processes that take place during curing. The dependence of the activation

TABLE IV
Curing Enthalpies for the Formulations Studied with 1 phr of BDMA

Formulation	$\Delta h_{\exp}$ (J g^{-1})	Δh_{theo} (J g^{-1})
DGEBA : TDI 2 : 1	450	405
DGEBA : TDI 1 : 1	590	580
DGEBA : TDI 1 : 2	620	640

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TABLE V
Kinetic Parameters of the Curing for Different DGEBA : TDI Formulations Catalyzed with 1 phr BDMA

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	DGEBA : TDI 2 : 1			DGEBA : TDI 1 : 1			DGEBA : TDI 1 : 2		
α	E (kJ mol^{-1})	ln[$AR/$ g(α)E] (s^{-1})	r	E (kJ mol^{-1})	ln[$AR/$ g(α)E] (s^{-1})	r	E (kJ mol^{-1})	ln[$AR/$ g(α)E] (s^{-1})	r
0.05	23.5	−0.76	0.9997	13.1	−4.68	0.9951	38.8	6.14	0.9999
0.1	18.0	−3.35	0.9922	10.8	−5.69	0.9999	33.6	3.71	1.0000
0.2	31.8	−0.02	0.9916	10.0	−6.35	0.9906	22.3	−1.18	0.9996
0.3	51.7	5.34	1.0000	21.3	−3.45	0.9920	19.2	−2.86	0.9957
0.4	45.0	2.99	0.9999	26.1	−2.53	0.9979	18.8	−3.60	0.9944
0.5	38.6	0.79	0.9999	27.7	−2.43	0.9997	35.0	0.32	0.9843
0.6	37.9	0.20	0.9997	34.4	−1.04	0.9998	52.4	4.27	0.9970
0.7	39.9	0.33	1.0000	37.4	−0.55	0.9988	61.5	5.85	0.9988
0.8	39.1	−0.21	0.9993	38.8	−0.48	0.9974	73.1	7.89	0.9992
0.9	35.9	−1.32	0.9985	41.2	−0.26	0.9966	98.5	12.79	0.9998
0.95	34.3	−1.89	0.9993	44.9	0.33	0.9975	120.0	16.85	1.0000

energy and reaction rate on the degree of conversion is represented in Figure 3 for formulation DGEBA/ TDI 1 : 1. Three regions of activation energy values (11.3, 23.7, and 37.4 kJ mol^{-1}) can be observed, in order of increasing degree of conversion or temperature, related to the three main DSC exotherms. The first region, where isocyanurate ring formation takes place, has an average activation energy of 11.3 kJ mol^{-1}. An average activation energy of 23.7 kJ mol^{-1} should be associated with the formation of oxazolidones and the homopolymerization of epoxides (second region). In the third region, the decomposition of isocyanurate rings increases the average activation energy until a value of 37.4 kJ mol^{-1}. The values of activation energy obtained are consistent with the fact that isocyanurate formation takes place at low temperature, epoxy homopolymerization and oxazolidone formation at intermediate temperature and isocyanurate decomposition to lead oxazolidones at high temperatures.

The value of activation energy of 23.7 kJ mol^{-1} is much lower than the obtained during the homopolymerization of neat DGEBA using tertiary amines different from BDMA, such as 1MI (60 kJ mol^{-1}) or DMAP (52 kJ mol^{-1}).[19] This result confirms that the tertiary amine/TDI zwitterion is the true active species in the initiation of DGEBA : TDI formulations instead of the tertiary amine/DGEBA zwitterion that leads to higher activation energies.

General characterization

Taking into account all the previous results we decided to study the isothermal curing and the final properties of the three DGEBA : TDI formulations using 1 phr of BDMA as the catalyst. To activate the different reactive processes, the polymerization was carried out in an oven in three stages: the first stage was achieved after 1 h at 80°C, then the samples

were put 15 h at 200°C and finally a postcuring at 250°C during 1 h was also applied.

By means of FTIR the final composition of the materials after isothermal curing were calculated (Table VI). It can be seen that an isocyanate excess favors isocyanurate formation, whereas an excess of epoxy favors the formation of oxazolidone, either directly by reaction between isocyanate and epoxy groups or by decomposition of isocyanurate rings at high temperatures. Homopolymerization of DGEBA is an important reaction even if an excess of isocyanate is used. This reaction should not be considered as secondary in any case, as some authors do,[2,6,7] and should be quantified to know the composition and a better understanding of the properties of the network formed.

Table VI shows that, by increasing the proportion of TDI the $T_{g\infty}$ strongly increases and the heat capacity step, $\Delta C_{p\infty}$, decreases. This result agrees with a higher crosslinking density n in formulations rich in isocyanurate rings (Table VI). However, the type of crosslinks and the stiffness can also contribute to the $T_{g\infty}$ value. It must be taken into account
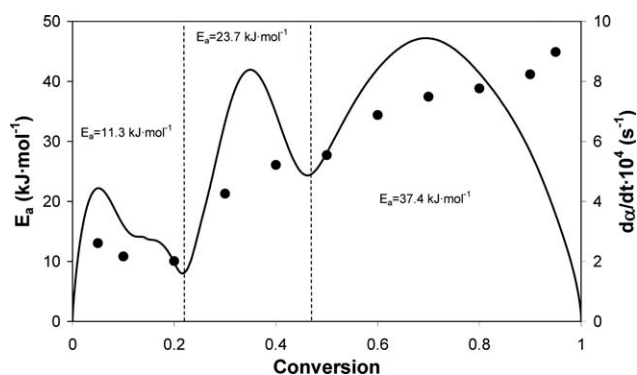

Figure 3 Dependence of activation energy (symbols) and reaction rate (line) on the degree of conversion for DGEBA : TDI 1 : 1 formulation catalyzed by 1 phr of BDMA.

TABLE VI
Calorimetric and TGA Data, Final Composition, Gelation, Densities, and Shrinkage of the Studied Systems

Formulation	T_{g0}^a (°C)	ΔC_{p0}^b (J g^{-1} K^{-1})	$T_{g\infty}^a$ (°C)	$\Delta C_{p\infty}^b$ (J g^{-1} K^{-1})	$T_{\tan\delta}^c$ (°C)	$T_{5\%}^d$ (°C)	Oxazol.^{e} (%)	Isocyanur.^{e} (%)	Ether^e (%)	n^f (mol kg^{-1})	F^f (g mol^{-1})	α_{gel}	ρ_0 (g cm^{-3})	ρ_∞ (g cm^{-3})	Shrinkage (%)
DGEBA : TDI 2 : 1	−24	0.59	145	0.33	151	360	42 (88)	6 (12)	54 (55)	2.6	25	12	1.179	1.275	7.5
DGEBA : TDI 1 : 1	−29	0.56	191	0.19	191	347	22 (37)	39 (63)	39 (63)	3.0	35	18	1.185	1.338	11.4
DGEBA : TDI 1 : 2	−46	0.55	239	0.12	261	331	13 (17)	55 (83)	22 (66)	3.3	48	24	1.193	1.352	11.8

1 phr of BDMA was used as catalyst in all formulations.
a Glass transition temperatures before and after isothermal curing obtained by DSC at 10°C min^{-1}.
b Difference in the heat capacity when the material changed from glassy to the rubbery state before and after isothermal curing obtained by DSC at 10°C min^{-1}.
c Temperature of the maximum of tan δ at 1 Hz.
d Temperature of a 5% of weight loss calculated by thermogravimetry.
e % of oxazolidone, isocyanurate and ether linkages present in the final network. In brackets % of oxazolidone, isocyanurate and ether formed respect to the initial isocyanate or epoxy content.
f Average crosslinking density, n, calculated assuming that homopolymerized DGEBA leads to two trifunctional crosslinks and an isocyanurate ring (3 isocyanate groups) forms another trifunctional crosslink. The chain stiffness, F, has been calculated considering the contribution of the different crosslinks and different chains present in the network as explained by Pascault et al.[19]

that there are at least two different types of crosslinks in the network, the isocyanurate rings and the ones coming from the homopolymerized DGEBA. In addition, the stiffness of the chains linked to the crosslinks can also differ: trimerized TDI > oxazolidone > DGEBA polyether (oxazolidone ring acts as a chain extender but is rigid and topologically bulky which hinders the network movement). A parameter F (network stiffness) has been calculated (see Table VI) taking into account the crosslinking density and the chain stiffness, according to the methodology proposed in the literature.[20] It can be seen that the stiffness of the network strongly increases with the initial TDI content of the formulation in good agreement with the increasing $T_{g\infty}$. Therefore, the flexibility and mobility of the different structures formed, polyether, polyisocyanurate, and polyoxazolidone have a strong contribution in the $T_{g\infty}$.

Gelation and shrinkage

In TMA, gelation is seen as a reduction in the oscillation amplitude because the gelified material is less deformable. This reduction is better observed in the signal derivative, as it can be seen in Figure 4 for DGEBA : TDI 1 : 1 formulation. Figure 4 shows how the gelation takes place at the beginning of the curing during the formation of isocyanurate rings (first exothermal peak in nonisothermal curing). Other formulations present similar behavior. Table VI shows that, by increasing the proportion of TDI and consequently the content of isocyanurate groups, the conversion at the gelation, α_{gel}, increases. Taking into account these results, it can be concluded that the gelation is controlled for isocyanate trimerization to form isocyanurate. As this process occurs at very low temperatures and in very short time, it is
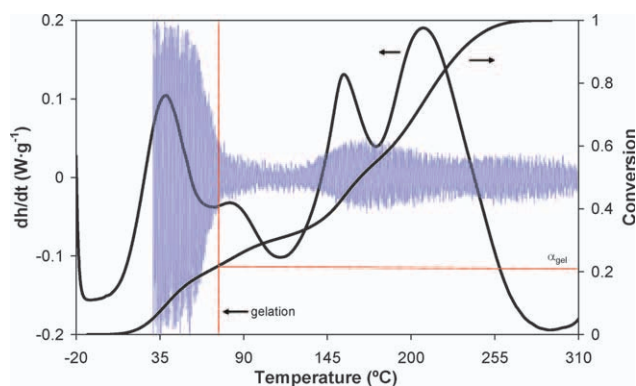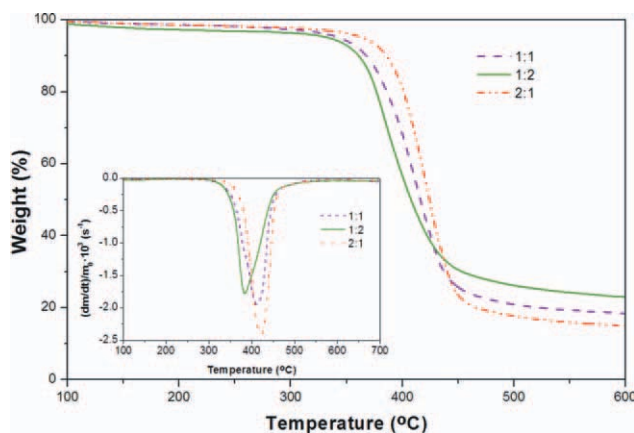

Figure 4 DSC thermograms and conversion for the DGEBA : TDI 1 : 1 formulation catalyzed with 1 phr of BDMA. TMA thermogram (derivative length in μm s^{-1} versus temperature) in blue color and determination of gelation are also included. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Figure 5 Thermogravimetric curves at 10 K min⁻¹ under nitrogen atmosphere for DGEBA : TDI formulations catalyzed by 1 phr of BDMA. The inset shows the rate of mass loss versus temperature. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

expected that this kind of materials have a very short pot-life and reduced processability.

It is also noticeable that in the region where the second and third exotherm appear the material becomes slightly more deformable, which can be related to the disappearance of isocyanurates and the corresponding formation of linear oxazolidone units.

Table VI shows how an increase in the amount of TDI produces an unwanted increase in the global shrinkage. This increase can be related with the reaction processes taking place during curing. In general, all reactive processes lead to shrinkage because the van der Waals distances between monomers convert into covalent bonds in the final material. Taking into account this criterion, it is expected the following order in the shrinkage: isocyanurate formation > oxazolidone formation > etherification, due to the fact that in isocyanurate formation three molecules react forming three new linkages; in oxazolidone formation two molecules react forming two new bonds, whereas in epoxy homopolymerization a bond is broken simultaneously to the formation of another one. Consequently, the higher shrinkage observed in 1 : 2 formulation than in 2 : 1 formulation can be related with the higher content of isocyanurate groups in TDI-rich formulation.

The fact that most of the shrinkage (related with formation of isocyanurate) takes place before gelation is beneficial for the material because shrinkage only produces internal stresses if it is generated in the solid state (after gelation).

Thermal stability

Figure 5 shows the thermogravimetric curves in nitrogen atmosphere of the DGEBA : TDI samples

and Table VI includes the temperature of the onset decomposition on the TGA calculated at a 5% of weight loss. When the TDI proportion is increased the thermal stability of the material decreases although all formulations are very stable. It is accepted that thermosets containing heterocyclic rings, such as isocyanurate and oxazolidone, have a high thermal stability.[5] Taking into account the final composition of the materials (Table VI), it seems that oxazolidone rings confer higher thermal stability than isocyanurate rings. Other factors, such as the degree of crosslinking and molecular interactions can also influence the thermal stability.

Dinamomechanical properties

Figure 6 shows the mechanical reaction spectra at 1 Hz for the formulations studied. As the proportion of TDI increases, the modulus–temperature curves move toward higher temperatures and the value of the relaxed modulus slightly increases (it is not possible to determine this modulus for 1 : 2 formulation since it appears at very high temperature, where the material begins to degrade). The tan δ curves are displaced accordingly to higher temperatures. The peak temperatures of the tan δ relaxation curve $T_{tan\,\delta}$, which can be often used as a measure of $T_{g\infty}$, are somewhat higher than the calorimetric $T_{g\infty}$, as seen in Table VI. The behavior of the relaxation spectra is consistent with the higher value of $T_{g\infty}$ revealed by DSC. Again, these results can be interpreted in terms of the crosslinking density and stiffness (n and F in Table VI). Homopolymerized DGEBA and isocyanurate rings lead to an increase in the crosslinking density, whereas oxazolidone rings are chain extenders but rigid and bulky groups that hinder mobility. The final temperature of glass transition and mechanical
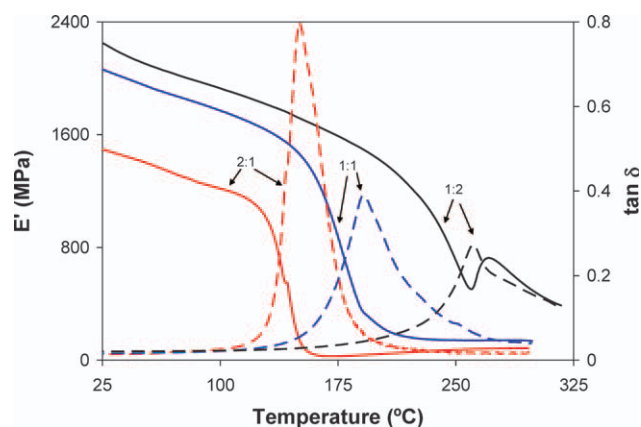
Figure 6 Temperature dependence of tan δ and storage modulus at 1 Hz for the DGEBA : TDI formulations catalyzed with 1 phr of BDMA. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

properties are a compromise between these two effects. Moreover, crosslinking density and chain stiffness also affect the damping behavior, which is related to the area under the loss tan δ curve. These areas have not been numerically evaluated, but the evolution can be qualitatively appreciated in the figure.

CONCLUSIONS

The curing of DGEBA with TDI using a tertiary amine as catalyst leads to materials with oxazolidone, isocyanurate, and ether groups in the chemical structure of the network. The initial composition of the formulation, the curing conditions, and the catalyst used are the parameters that control the final structure of the network formed, the evolution of the curing, and the final properties of the thermosets. The modification of these parameters allows obtaining tailor-made materials with the desired characteristics.

At low temperature (below 100°C) isocyanurate formation, that controls the gelation, is the only reaction taking place. At intermediate temperatures (between 110 and 190°C) two reactions compete, oxazolidone formation and epoxy homopolymerization and at high temperatures (above 190°C) isocyanurate decomposition to form oxazolidone rings is the main reaction taking place although thermal epoxy homopolymerization can also occur. When BDMA is used as the catalyst in the curing of DGEBA : TDI formulations, the zwitterion formed between tertiary amine and isocyanate is the only active species.

Isocyanurate-rich formulations have higher glass transition temperature and shrinkage, whereas the formation of oxazolidone increases the thermal sta-

bility. The content in ether linkages, even in TDI-rich formulation, is another factor that tunes the properties and should be taken into account to establish the structure–properties relationship.

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