Available online at www.sciencedirect.com

SCIENCE DIRECT®

Polymer 46 (2005) 7989–8000

polymer

www.elsevier.com/locate/polymer

Mechanistic kinetic model of an epoxy resin cured with a mixture of amines of different functionalities

Miren Blanco[a], M. Angeles Corcuera[a], Carmen C. Riccardi[b], Iñaki Mondragon[a,*]

[a]*Materials and Technologies Group, Dpto. Ingeniería Química y Medio Ambiente, Escuela Universitaria Politécnica, Universidad País Vasco/Euskal Herriko Unibertsitatea, Plaza Europa 1, 20018 Donostia/San Sebastián, Spain*

[b]*Institute of Materials Science and Technology (INTEMA), University of Mar de Plata and National Research Council (CONICET), Av. Juan B. Justo 4320, 7600 Mar de Plata, Argentina*

Received 19 October 2004; received in revised form 16 May 2005; accepted 27 June 2005

Abstract

The polymerization kinetics of a monoamine (*p*-toluidine), a diamine (4,4′-diaminodiphenylmethane) or a mixture of both amines reacted with an epoxy prepolymer, diglycidylether of bisphenol A (DGEBA), was analyzed using differential scanning calorimetry. A simple mechanistic model, consisting of an epoxy–hydroxyl complex formation out of equilibrium, including the possibility that amino hydrogens react with free epoxy groups or with the epoxy–hydroxyl complex, and taking into account the possible difference of the reactivity of amino hydrogens, provided a reasonable fitting of the whole set of experimental results with a lonely set of activation energies.

Keywords: Thermosets; Kinetic; Mechanistic model

---

1. Introduction

Epoxy resins are reactive monomers, which are transformed by curing in thermosetting polymers. Owing to their performance properties, they are extensively used in many applications such as coatings, adhesives, laminates and matrices for composite materials and structural components. It is possible to tailor and improve polymer properties for specific applications, choosing between the wide variety of curing agents and epoxy resins available. The functionality of the reactants controls the development and the crosslink density of the network. In this way, it is possible to construct networks of controlled architecture, by only modifying the molecular weight between crosslinks ($\bar{M}_c$). One way to achieve this modification [1] is by reacting a bifunctional epoxy resin with a mixture of amines of different functionalities, one of which being a monoamine that plays the role of a chain extender. Several works have been published studying these epoxy–amine mixtures. Most of them have focused on the effects of network architecture on their thermal and mechanical behaviour and not on the kinetic features involved in the formation of networks [2–8]. These features are of great practical importance since optimization of processing requires a reliable kinetic model including reactions which take place during polymerization.

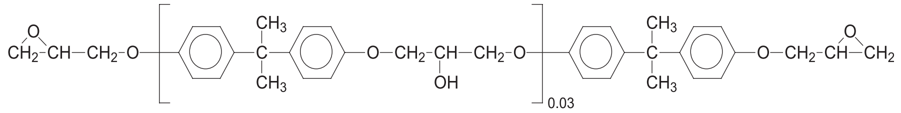
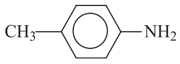
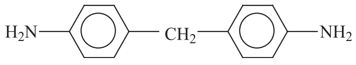
Kinetic mechanisms of epoxy resin curing have been intensively studied in the past applying different models, methods and experimental techniques. Modelling of the curing process can be approached both mechanistically and phenomenologically. Phenomenological models are based on empirical or semi-empirical rate laws which explain the well-known autocatalytic behaviour of the epoxy–amine reaction. They are widely employed because they are simple and fit isothermal data with relative success, but do not fit consistently dynamic thermograms [9] and results obtained from them cannot be extrapolated to new initial compositions or curing conditions [10]. In this regard, mechanistic models have been developed. They account for the individual species concentrations and offer more flexibility to changes in formulation, because such models consider the complete scheme of consecutive and competitive reactions, which take place during curing. The principal disadvantage of these mechanistic models is the need for an accurate description of all species and reactions involved in the

---

* Corresponding author. Tel.: +34 943 017271; fax: +34 943 017200. *E-mail address:* iapmoegi@sc.ehu.es (I. Mondragon).

0032-3861/$ - see front matter © 2005 Elsevier Ltd. All rights reserved.
doi:10.1016/j.polymer.2005.06.117

Table 1
Monomer structure, characteristics and nomenclature

Monomer	Formula	Molar mass ($g\ mol^{-1}$)	Melting point (°C)
Diglycidyl ether of bisphenol A		349	45
p-Toluidine		107	43
4,4′-Diamino diphenyl methane		198	80

system, which depend on the reactants utilized and on their curing conditions. This can create difficulty when analysing.

In order to provide a better understanding of the kinetic features involved in curing processing of an epoxy prepolymer and an amine mixture of different functionalities, this work arises to obtain the simplest and most reliable mechanistic kinetic model needed to fit the experimental results obtained by means of differential scanning calorimetry.

2. Experimental

2.1. Materials

The epoxy monomer used in this study was DER332, a difunctional diglycidyl ether of bisphenol A (DGEBA), kindly supplied by Dow Chemical. It has an equivalent weight of around 175 g/equiv and a hydroxyl/epoxy ratio of 0.015. The curing agent was 4,4′-diaminodiphenylmethane (DDM), Ciba-Geigy HT972, a solid difunctional aromatic amine with a molecular weight of 198 g/mol. A solid monofunctional aromatic primary amine, *p*-toluidine, Fluka, with a molecular weight of 107 g/mol, was used as a chain extender. DER332 was placed in a vacuum oven at 80 °C overnight to remove any water present and amines were used as received without purification. Both of the amines have a similar chemical structure to ensure similar composition of the resultant products (Table 1).

2.2. Sample preparation

Two series of mixtures were used. The first one was prepared mixing only the monofunctional amine with the epoxy resin at 50 °C for 5 min. Mixtures with various stoichiometric ratios between the epoxide group and the active hydrogens of the amine, $r=1$, 0.75 and 0.5 were obtained. The second series was carried out adding DDM and *p*-toluidine/DDM mixtures to the epoxy resin at 80 °C stirring vigorously for 5 min. For this series, amines and resin were mixed keeping stoichiometric ratio. Mixtures of amines were carried out at the following ratios of monoamine:diamine equivalents: 0.33:1, 1:1 or 1:0.33. A fresh sample of all systems was prepared before every experimental determination.

2.3. Differential scanning calorimetry (DSC)

DSC measurements were carried out in a Mettler Toledo DSC 821e module equipped with an intracooler, and previously calibrated with high purity indium and zinc standards. Experiments were conducted in a dry atmosphere, working with 5–10 mg samples. Runs at a constant heating rate of 10 °C/min were performed in a temperature range from −60 to 250 °C for every sample. Kinetic studies were also performed with the DSC equipment working isothermally at temperatures ranging from 80 to 110 °C. All the samples were then cooled to room temperature and subjected to a dynamic DSC scan from 30 to 250 °C at 10 °C/min to determine the residual heat of reaction. In a second dynamic scan the glass transition temperature of the fully cured material, $T_{g\infty}$, was determined. $T_{g\infty}$ was taken as the middle point of the endothermic shift. Conversion, x, was taken as the heat of reaction calculated from the isothermal mode at each cure time, divided by the total heat of reaction obtained from the addition of the total heat from the isothermal mode to the residual one for each system.

Owing to the high vapor pressure of *p*-toluidine, sealed aluminium pans were used. To ensure evaporation of the amine was controlled, thermogravimetric analyses of some pans were carried out in a Setaram thermoanalyser model 92, in a helium atmosphere. Measurements performed in both the scanning mode from room temperature to 250 °C at 10 °C/min and the isothermal mode at the highest temperature employed revealed no significant mass loss.

2.4. Gel permeation chromatography (GPC)

The number-average molecular mass $\bar{M}_n$, the mass average molecular mass $\bar{M}_w$ and the molecular weight distributions $\bar{M}_w/\bar{M}_n$ of the obtained linear polymers were determined using a Perkin–Elmer LC-295 gel permeation chromatograph, equipped with a refractive index detector and three Waters Styragel columns of 100, 500 and 10^4 Å

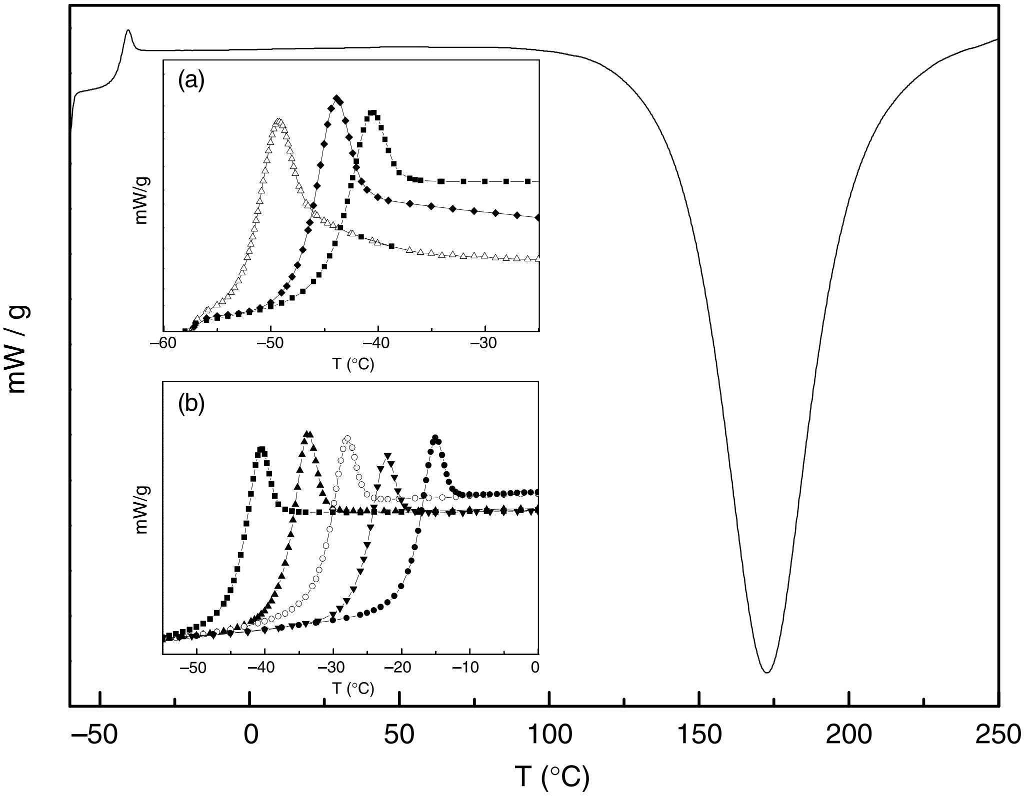


Fig. 1. General shape of dynamic thermograms for all systems and details of T_{g0} region for: (a) DGEBA with *p*-toluidine at different epoxy/amine stoichiometric ratios: (■) 1, (◆) 0.75, and (△) 0.5; (b) stoichiometric DGEBA/amine mixtures containing several *p*-toluidine:DDM ratios: (■) 1:0, (▲) 1:0.33, (○) 1:1, (▼) 0.33:1 and (●) 0:1.

nominal pore sizes which had molecular weight ranges of 100-5×10^3, 500-2×10^4 and 5×10^3–6×10^5 g/mol, respectively. The eluent used was tetrahydrofuran (THF) at a flow rate of 1 mL/min. All molecular weight reported are based on a calibration curve from narrow distribution polystyrene standards, therefore, results are expressed as polystyrene equivalent molecular weights.

3. Results and discussion

The cure kinetics of both series of epoxy–amine mixtures was studied by differential scanning calorimetry in dynamical and isothermal modes. All dynamic scans had a similar shape, as represented in Fig. 1. The curve shows a step in the heat flow at low temperatures, due to glass transition from the glassy to the liquid state of the unreacted mixture, T_{g0}. Fig. 1(a) and (b) illustrates that an increase in the amount of *p*-toluidine results in the decrease of the initial T_{g0} of the mixtures. The low molecular weight *p*-toluidine acts as a plasticizer. As temperature increases, the epoxy–amine reaction transforms the initial mixture in a higher molecular weight system, thus giving rise to the exothermic peak.

For the first series, major changes caused by the reaction in the epoxy–monoamine systems were an increase in molecular weight and glass transition temperature which resulted in a linear structure of molecular masses ranging from $\bar{M}_w \approx 1127$ g/mol for the mixture with more excess of amine to 47,801 g/mol for the stoichiometric mixture and $T_{g\infty}$ ranging from 297.5 to 365 K. The main characteristics of the resultant linear polymers, obtained by GPC, are collected in Table 2. Regarding the heat of reaction values, they are in the usual range of values reported in the literature survey [11–13]. In agreement with other authors [14,15], mixtures with monoamine excess present slightly higher

Table 2
Results of dynamic DSC and GPC measurements for DGEBA/*p*-toluidine mixtures at different epoxy/amine stoichiometric ratios

r	e_0 (equiv/L)	T_{g0} (K)	T_{peak} (K)	$T_{g\infty}$ (K)	ΔH (kJ/equiv)	$\bar{M}_n$ (g/mol)	$\bar{M}_w$ (g/mol)	$\bar{M}_w/\bar{M}_n$
1	5.01	231.0	446.0	365.0	102.4	19,400	47,800	2.5
0.75	4.62	228.0	443.0	342.5	107.3	3100	5700	1.8
0.5	3.99	222.0	436.0	313.0	108.4	1000	1100	1.1

The initial epoxy concentration of each mixture is also shown.

Table 3
Results of the dynamic DSC measurements and characteristics of stoichiometric mixtures of DGEBA with several *p*-toluidine:DDM ratios

p-Toluidine: DDM	e_0 (equiv/L)	T_{g0} (K)	$T_{\rm peak}$ (K)	$T_{g\infty}$ (K)	ΔH (kJ/equiv)	$\bar{M}_c$ (g/mol)	$x_{\rm gel}$
1:0	5.01	231.0	446.0	365.0	102.4	Linear polymer	–
1:0.33	4.86	238.0	445.0	381.0	105.2	1799	0.82
1:1	4.71	243.5	444.0	395.0	101.6	896	0.71
0.33:1	4.58	249.0	441.0	410.0	100.1	594	0.63
0:1	4.45	256.5	442.0	445.5	100.0	444	0.58

The initial epoxy concentration of each mixture is also shown.

values and react faster than equimolar one (Fig. 2). This behaviour is explained below.

In the second series, systems with DDM and mixtures of *p*-toluidine and DDM were investigated. Thus, besides the molecular weight increases gelation and network formation occurred as well. In Table 3, the initial epoxy concentration of each mixture (e_0), the results of the dynamic DSC measurements, the theoretical values of the extent of reaction at which gelation occurs ($x_{\rm gel}$), and also the theoretical molecular weight between crosslinks ($\bar{M}_c$) are summarized. Based on the Flory's theory, $x_{\rm gel}$ was calculated supposing that the rate constants for primary and secondary amine addition are equal. The equation employed is expressed as follows:

$$x_{\rm gel} = \left[\frac{r}{(f_e-1)\left(\sum_{f_a=2}^{\infty}\Phi_{f_a}(f_a-1)\right)}\right]^{1/2} \qquad (1)$$

where r is the epoxy/amine stoichiometric ratio, Φ_{f_a} is the mole fraction of amine hydrogens provided by the f_a-th functional amine and f_e and f_a are the epoxy and amine functionalities, respectively. $\bar{M}_c$ of these stoichiometric mixtures was also calculated by assuming full conversion by the following equation previously employed by Lesser and Crawford [3–5]:

$$\bar{M}_c = \frac{2\left(M_e + \sum_{f_a=2}^{\infty}\frac{M_{f_a}}{f_a}\Phi_{f_a}\right)}{\sum_{f_a=3}^{\infty}\Phi_{f_a}} \qquad (2)$$

where M_e is the epoxy equivalent weight of the resin and M_{f_a} is the molecular weight of the f_a-th functional amine. Φ_{f_a} and f_a have been defined already.

As expected, increasing the amount of the monoamine not only increased the conversion value at which gelation occurs, but also the molecular weight between crosslinks in the networks and therefore, the values of $T_{g\infty}$ decreased. Owing to the similar chemical nature of amine structures, differences in their $T_{g\infty}$ are basically a result of differences in crosslinking density.

The heat of reaction values, represented in Table 3, are in close agreement with other results reported in the literature survey [9,11,12]. Slightly lower values are obtained for more crosslinked systems, maybe because topological restrictions caused by crosslinking hinders the reaction of all the functional groups present in the system. The higher flexibility of networks with a higher monoamine content

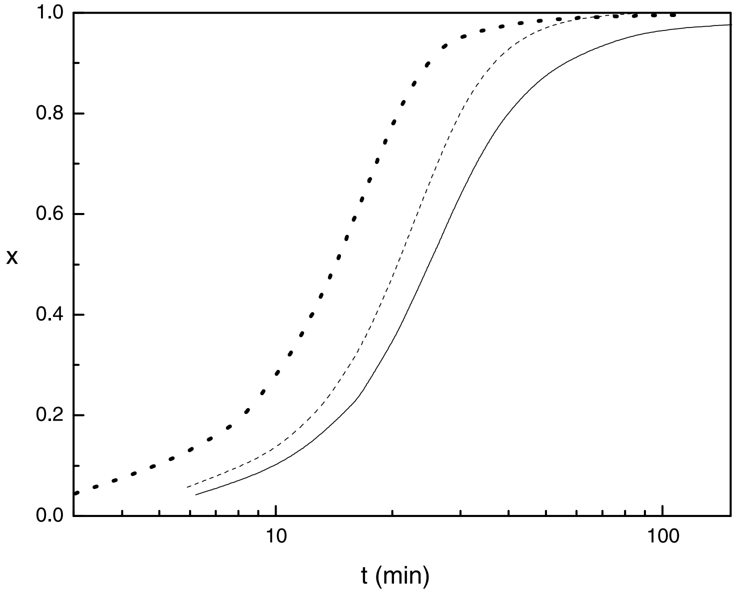


Fig. 2. Conversion versus time profiles at 110 °C for DGEBA/*p*-toluidine mixtures with different epoxy/amine stoichiometric ratios: (—) $r=1$, (- - -) $r=0.75$, and (···) $r=0.5$.

seems to overcome this effect. The similarity of the heat of reaction values for both series of mixtures and the thermograms shape indicate that similar chemical reactions occurred even though the polymerization rate was different. Hence, a common mechanism for the epoxy matrix polymerization can be used to describe the behaviour of all mixtures.

Polymerization kinetics of these systems was also studied at different isothermal temperatures ranging from 80 to 110 °C. Values of reaction heats were obtained from dynamic runs and from the sum of the isothermal heat of reaction and the residual heat obtained in the subsequent scan. The constancy of the experimental values of total heat of reaction under different curing conditions furnishes indirect proof that monoamine volatilization during the reaction was not significant. Typical plots of x versus time are reported in Figs. 3–5, whose shape clearly evidences the autocatalytic nature of the process. In this study, a simple and accurate kinetic model has been developed to explain the reaction behaviour.

4. Model development

As outlined above, this work arises to obtain a simple and reliable mechanistic kinetic model to fit the results for the polymerization of an epoxy prepolymer and amine mixtures of different functionalities. Firstly, the study was restricted to the polyaddition reaction with the monoamine at epoxy/amine stoichiometric ratios, $r=1$, 0.75 and 0.5 (amine excess). Taking into account that full epoxy conversion was achieved during the formation of these linear polymers, the influence of other physical process such as vitrification could be neglected simplifying the kinetic analysis. Furthermore, knowing that etherification reactions are not important at low temperatures for stoichiometric mixtures or for amine excess [16–19], and that catalytic effects toward homopolymerization of the sterically hindered tertiary amines are not significant [11], both of these reactions have been excluded from the analysis. Many kinetic models exist which include the assumption, originally derived by Smith [20], that the oxirane ring is activated to a pre-equilibrium state by hydrogen bonding between the oxygen of the epoxide and any proton donor. Most of authors assume that such equilibrium is achieved at a very fast rate, so that the complex has an Arrhenius behaviour, being its concentration in equilibrium with the epoxy and the hydroxyl groups, thus simplifying the kinetic evaluation by using the corresponding equilibrium constant. One of these models, previously reported by Riccardi et al. [21], was unsuccessfully tested using the experimental results. Flammersheim et al. [15] worked with a similar model, also derived from the Smith mechanism, obtaining a similar conclusion for another epoxy–monoamine system. They solved the problem by considering that different hydrogen bonded transition complexes may be formed, whose formation and dissociation during the reaction control the kinetics. So, they included in the kinetic scheme the formation of the three complexes E–OH, E–A and A–OH, firstly suggested by Mijovic et al. [22,23], obtaining a very good fitting of experimental results. The existence of other complexes such as A–A and OH–OH was neglected in the model. Nevertheless, the high number of equations in

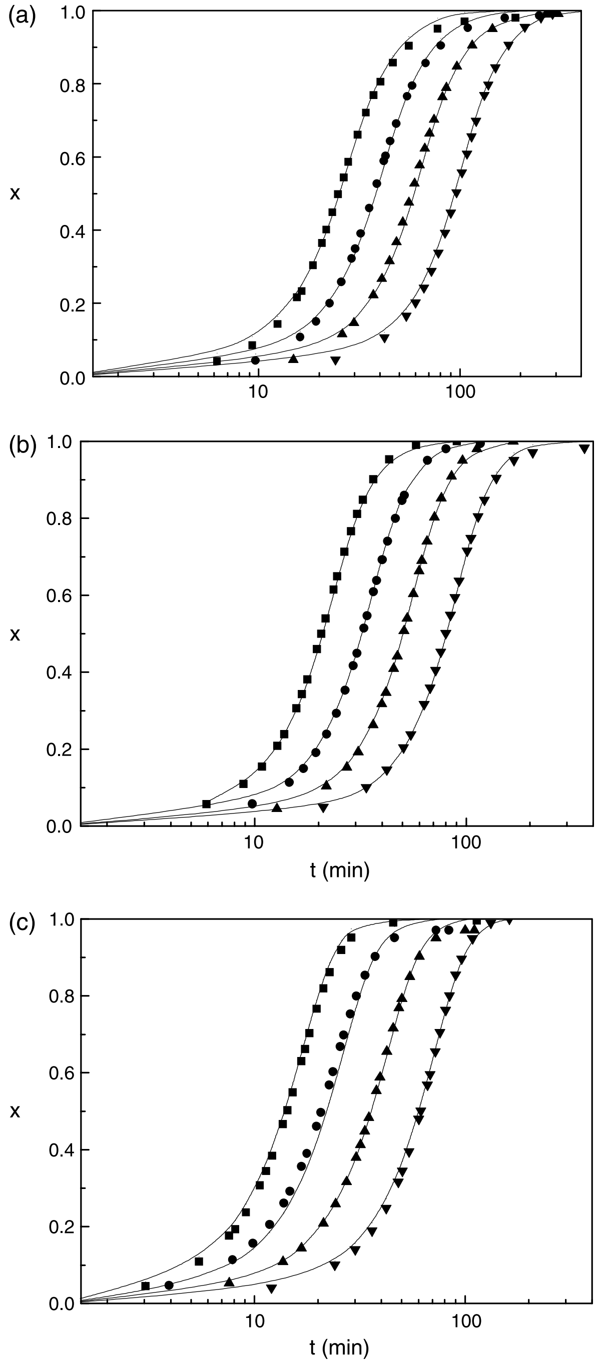


Fig. 3. Isothermal conversion versus time profiles for DGEBA/*p*-toluidine mixtures with different epoxy/amine stoichiometric ratios: (a) 1, (b) 0.75, and (c) 0.5. Temperatures employed are: (▼) 80 °C, (▲) 90 °C, (●) 100 °C, and (■) 110 °C. The solid lines represent the theoretical prediction of the mechanistic kinetic model.

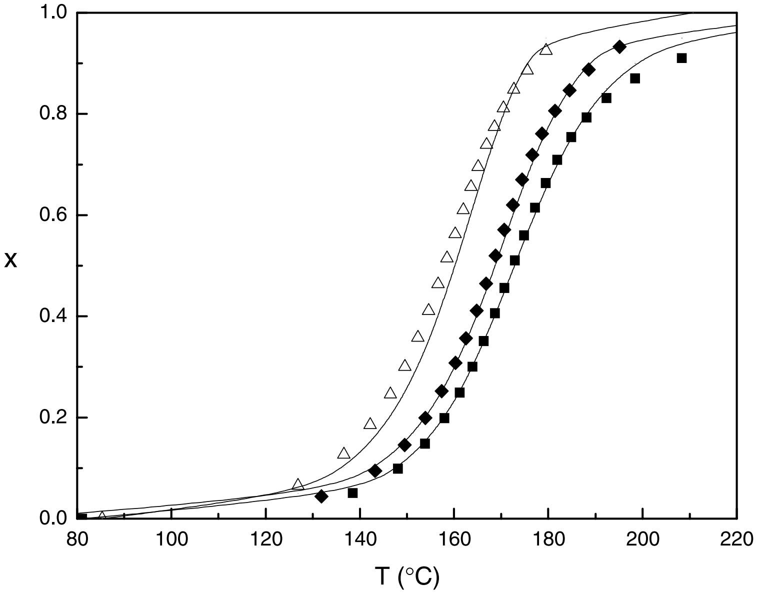


Fig. 4. Dynamic conversion versus temperature profiles for DGEBA/*p*-toluidine mixtures with different epoxy/amine stoichiometric ratios: (■) 1, (◆) 0.75, and (△) 0.5. The solid lines represent the theoretical prediction of the mechanistic kinetic model.

the reaction scheme involves a great number of adjustable parameters, making its use unreliable under different experimental conditions.

The stability of E–OH complex depends on the relation between the rate at which the intermediate gives final products and the rate of the backward reaction [24]: if the complex reacts with the amine at a reaction rate not small in comparison with the backward reaction, the complex shows a Van't Hoff behaviour and thus, it is possible to consider a stationary state approach; on the contrary the complex shows an Arrhenius behaviour and its concentration is the corresponding to the equilibrium. To obtain a simple and accurate kinetic model maintaining the existence of E–OH as the only intermediate complex, we have assumed that the complex formation does not achieve the equilibrium quickly, so that rate equations for the forward and backward reactions have to be considered.

According to this assumption, the following reaction scheme can be written by denoting E = epoxy group, OH = hydroxyl group, E–OH = complex between epoxy and hydroxyl groups, and A_1, A_2, A_3 = primary, secondary and tertiary amines, respectively:

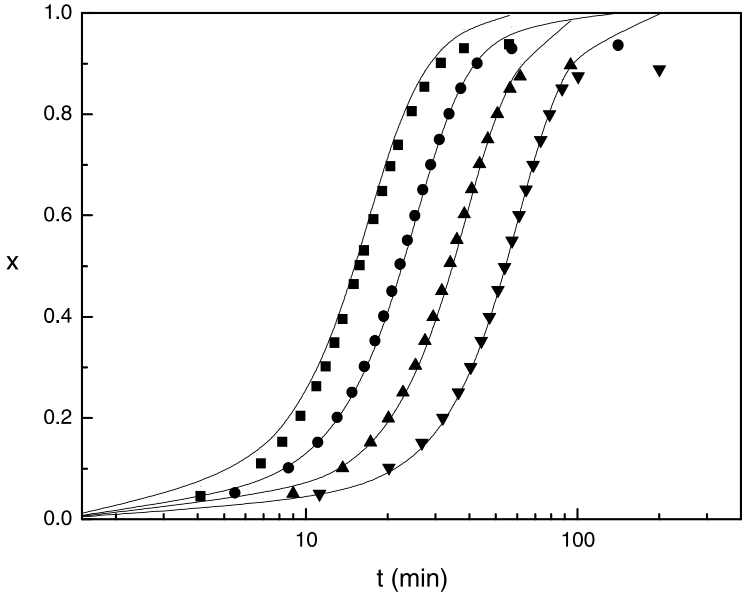


Fig. 5. Isothermal conversion versus time profiles for stoichiometric DGEBA/DDM mixtures at different temperatures: (▼) 80 °C, (▲) 90 °C, (●) 100 °C, and (■) 110 °C. The solid lines represent the theoretical prediction of the mechanistic kinetic model.

$$\mathrm{E} + \mathrm{OH} \underset{k'}{\overset{k}{\rightleftharpoons}} \mathrm{E{-}OH}$$

$$\mathrm{E} + \mathrm{A}_1 \xrightarrow{k_1} \mathrm{A}_2 + \mathrm{OH}$$

$$\mathrm{E} + \mathrm{A}_2 \xrightarrow{k_2} \mathrm{A}_3 + \mathrm{OH}$$

$$\mathrm{E{-}OH} + \mathrm{A}_1 \xrightarrow{k'_1} \mathrm{A}_2 + 2\mathrm{OH}$$

$$\mathrm{E{-}OH} + \mathrm{A}_2 \xrightarrow{k'_2} \mathrm{A}_3 + 2\mathrm{OH}$$

It has been assumed that the reactivities of both epoxy groups in the epoxy resin are identical and independent.

As previously pointed out, the complex formation represented by the first equation is out of equilibrium, so that rate equations for the forward and backward reactions have to be stated through the rate constants k and k', respectively. The specific rate constants k_1 and k_2 correspond to the reactions catalyzed by hydroxyl groups and impurities initially present in the formulation; the specific rate constants k'_1 and k'_2 indicates the reaction of the epoxy–hydroxyl complex with amine hydrogens.

The ratio of secondary to primary monoamine hydrogen rate constants, N, is assumed to be constant and independent of temperature. The assumption made by Horie et al. [12], which states that the ratio is the same for both the hydroxyl-catalyzed and the impurity catalyzed reactions, was maintained:

$$N = \frac{k_2}{k_1} = \frac{k'_2}{k'_1} \tag{3}$$

Normalized constants respect to the initial epoxy concentration e_0, shown in Table 2, can be defined as $K = ke_0$, $K' = k'$, $K_1 = k_1 e_0$, $K_2 = k_2 e_0$, $K'_1 = k'_1 e_0$, $K'_2 = k'_2 e_0$. They have time^{-1} units. Denoting x as the epoxy conversion and e, e–oh, a_1, a_2, a_3 and Oh, as the corresponding molar concentrations of the different groups, made dimensionless by dividing with the initial molar concentration of epoxy groups, the reaction kinetics may be expressed by the following set of differential equations:

$$\frac{\mathrm{d}e}{\mathrm{d}t} = -Ke\mathrm{Oh} + K'e\text{–oh} - K_1 e(a_1 + Na_2) \tag{4}$$

$$\frac{\mathrm{d}e\text{–oh}}{\mathrm{d}t} = Ke\mathrm{Oh} - K'e\text{–oh} - K'_1 e\text{–oh}(a_1 + Na_2) \tag{5}$$

$$\frac{\mathrm{d}a_1}{\mathrm{d}t} = -2a_1(K_1 e + K'_1 e\text{–oh}) \tag{6}$$

$$\frac{\mathrm{d}a_2}{\mathrm{d}t} = (K_1 e + K'_1 e\text{–oh})(a_1 - Na_2) \tag{7}$$

$$\frac{\mathrm{dOh}}{\mathrm{d}t} = -Ke\mathrm{Oh} + K'e\text{–oh} + (K_1 e + 2K'_1 e\text{–oh})(a_1 + Na_2) \tag{8}$$

and the conversion at each time is calculated as:

$$x = 1 - e - e\text{–oh} \tag{9}$$

A Runge–Kutta method was applied to Eqs. (4)–(8), assuming that at the beginning of the reaction there was 0.015 equiv OH/equiv epoxy coming from the epoxy molecule, $a_2 = 0$ and $e\text{–oh} = 0$. It is important to point that according to previous works [25,26], the best results are achieved considering the same reactivity of primary and secondary amine hydrogens, $N = 1$. K, K', K_1 and K'_1 are expressed as a function of temperature in terms of an Arrhenius equation:

$$k = A \exp\left(\frac{-E_\mathrm{a}}{RT}\right) \tag{10}$$

where A is the preexponential factor, E_a the activation energy, R the gas constant and T the absolute temperature.

As shown in Fig. 3, the model fits successfully curves of curing with the monoamine for the whole range of temperatures and stoichiometric ratios employed. The goodness of the fitting, with the same kinetic parameters, for corresponding dynamic runs is shown in Fig. 4. Dimensional kinetic rate parameters are summarized in Table 4. These values indicate that the rate constant for the reaction of E–OH with the amine (k'_1) is higher than that of the dissociation of the complex (k') confirming that E–OH has a Van't Hoff complex behaviour. As reported by other authors, the non-catalytic reaction was not significant. The amine excess seems to increase slightly its value, possibly because the amount of hydroxyl groups and impurities initially present in the formulation increases with the monoamine content. The ratio between k and k' shows that the formation of E–OH complex seems to be enhanced

Table 4
Dimensional kinetic rate parameters of the obtained mechanistic model for the reaction of DGEBA with *p*-toluidine at various epoxy/amine stoichiometric ratios

	A			E_a (kJ/mol)
	$r=1$	$r=0.75$	$r=0.5$	
A_k (L/equiv min)	9.61×10^6	1.42×10^7	2.01×10^7	58.2
$A_{k'}$ (1/min)	2.37×10^7	1.63×10^7	6.75×10^6	77.9
A_{k_1} (L/equiv min)	4.27×10^5	4.44×10^5	9.75×10^5	64.9
$A_{k'_1}$ (L/equiv min)	2.33×10^4	1.83×10^4	1.52×10^4	41.4

Table 5
Dimensional kinetic rate parameters obtained with the applied mechanistic model for reaction of stoichiometric DGEBA/amine mixtures containing several *p*-toluidine:DDM ratios

p-Toluidine:DDM ratio	A_k (L/equiv min)	$A_{k'}$ (1/min)	$A_{k_{1M}}$ (L/equiv min)	$A_{k'_{1M}}$ (L/equiv min)	$A_{k_{1D}}$ (L/equiv min)	$A_{k'_{1D}}$ (L/equiv min)
1:0	9.61×10^6	2.38×10^7	4.28×10^5	2.33×10^4	–	–
1:0.33	1.99×10^7	8.22×10^7	1.94×10^5	2.79×10^4	2.36×10^5	2.79×10^4
1:1	8.87×10^6	4.16×10^7	2.48×10^5	2.85×10^4	4.94×10^5	3.55×10^4
0.33:1	5.77×10^6	4.25×10^7	1.65×10^6	5.85×10^4	2.24×10^5	5.98×10^4
0:1	9.35×10^6	6.3×10^7	–	–	3.76×10^5	4.14×10^4

by the presence of amine excess. The higher amount of the E–OH complex available for the reaction with the amine allows to understand the faster reaction observed in Fig. 2 for non-stoichiometric mixtures, even though the value of k'_1 decreases slightly.

In each step of the model, a common value of activation energy was found for all the epoxy/amine stoichiometric ratios analyzed. Values of activation energy for the hydroxyl-catalyzed (E'_1) and for the impurity catalyzed reactions (E_1) were in agreement with the available information concerning epoxy–amine reactions at low temperatures [12].

With the aim of proving the validity of this model, it was also applied to the curing reaction of a widely studied system (DGEBA/DDM). The ratio of the reactivities between the secondary and the primary amine hydrogens in this diamine has been the subject of many studies and the value of 0.65 previously found by Girard-Reydet et al. [27,28] has been established. The difference in the N value between the mono and the diamine, taking into account the similarity of their chemical structures, can be attributed to the more flexible product obtained with the monoamine: a linear polymer. This fact is in agreement with the change in N produced when an aromatic diamine is replaced with an aliphatic one in a DGEBA/diamine system [9,21]. In addition, DGEBA reacts with the diamine at a higher rate than with the monoamine. This fact has also been reported by other authors [29–31] and it has been attributed to the additional aminophenyl group in DDM which increases the electronegativity on nitrogen making the amine more reactive [29]. The same values of activation energies obtained for the epoxy–monoamine systems were maintained in each step of the model. The preexponential factors are shown in Table 5. Values of activation energies for the hydroxyl-catalyzed and for the impurity catalyzed reactions were in agreement with those reported in the literature for the same system [28,32]. Small differences with regard to published values can be attributed to the application of a different scheme of reaction, since each step of the model is dependent on the previous and simultaneous reactions. The kinetic model, as it is shown in Figs. 5 and 6, fits equally well both isothermal and dynamic experimental results for the whole previtrification stage where the reaction is chemically controlled, thus confirming its validity. Thereafter, in the vitrification region, the kinetic model fails and diffusion control becomes influential. Some models exist for

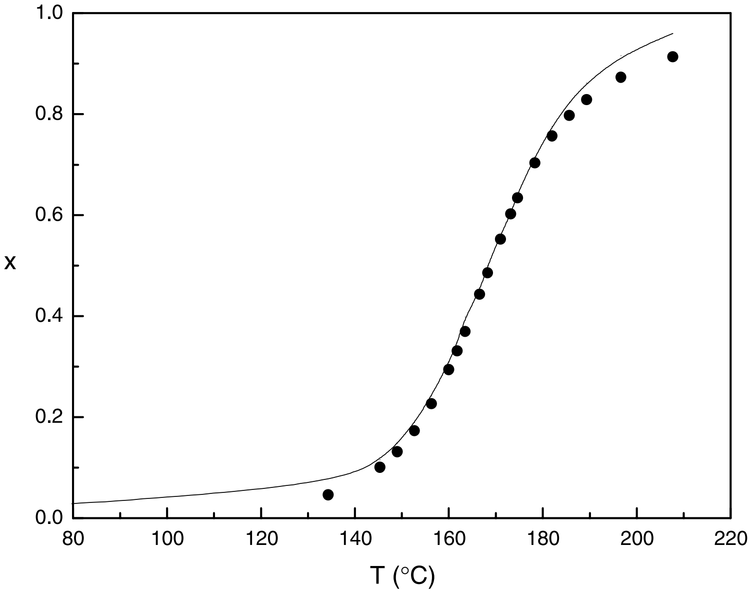


Fig. 6. Dynamic conversion versus temperature profiles for stoichiometric DGEBA/DDM mixture. The solid line represents the theoretical prediction of the mechanistic kinetic model.

analysing the diffusion controlled regime but they have not been used in this study [19,29,30,33].

Then, the reaction scheme was extended to obtain a unique kinetic model to describe the behaviour of a stoichiometric epoxy–amine system made up of a mixture of both monoamine and diamine with an epoxy prepolymer. Different reactivities of monoamine and diamine hydrogens were considered, obtaining a scheme of eight steps, which dimensionless specific rate constants K_{1M}, K_{2M}, K_{1D} and K_{2D}, corresponding to the reaction catalyzed by hydroxyl groups and impurities initially present in the formulation for the monoamine and the diamine, respectively; and the dimensionless specific rate constants K'_{1M}, K'_{2M}, K'_{1D} and K'_{2D} indicate the reaction of the epoxy–hydroxyl complex with amine hydrogens. The ratio of secondary to primary monoamine hydrogen rate constants N_M, and the ratio of secondary to primary diamine hydrogen rate constants N_D were assumed to be constant, independent of temperature and equal to 1 and 0.65, respectively.

The molar concentrations of the different groups are dimensionless by dividing with the initial molar epoxy groups concentration. Hence, the reaction kinetics for a stoichiometric system may be expressed by the following set of differential equations:

$$\frac{de}{dt} = -Ke\mathrm{Oh} + K'e\text{–oh} - K_{1M}e(m_1 + N_M m_2) - K_{1D}e(d_1 + N_D d_2) \quad (11)$$

$$\frac{de\text{–oh}}{dt} = Ke\mathrm{Oh} - K'e\text{–oh} - K'_1 e\text{–oh}(m_1 + N_M m_2) - K'_{1D}e\text{–oh}(d_1 + N_D d_2) \quad (12)$$

$$\frac{dm_1}{dt} = -2m_1(K_{1M}e + K'_{1M}e\text{–oh}) \quad (13)$$

$$\frac{dm_2}{dt} = (K_{1M}e + K'_{1M}e\text{–oh})(m_1 - N_M m_2) \quad (14)$$

$$\frac{dd_1}{dt} = -2d_1(K_{1D}e + K'_{1D}e\text{–oh}) \quad (15)$$

$$\frac{dd_2}{dt} = (K_{1D}e + K'_{1D}e\text{–oh})(d_1 - N_D d_2) \quad (16)$$

$$\frac{d\mathrm{Oh}}{dt} = -Ke\mathrm{Oh} + K'e\text{–oh} + (K_{1M}e + 2K'_{1M}e\text{–oh}) \times (m_1 + N_M m_2) + (K_{1D}e + 2K'_{1D}e\text{–oh}) \times (d_1 + N_D d_2) \quad (17)$$

where m_1 and d_1 are the dimensionless concentration of primary amine equivalents and m_2 and d_2 those of the secondary amine ones for the mono (m) and diamine (d) groups. The conversion is calculated with Eq. (9).

The fitting of the proposed kinetic model with experimental data is shown in Figs. 7 and 8. The model provides a good agreement with the experimental curves, but some deviation attributed to vitrification is observed at high conversions. This deviation is more important at low curing temperatures and as the amount of diamine increases because the $T_{g\infty}$ of the system also increases, thus becoming more important the influence of vitrification. Values of activation energies have also been maintained constant in

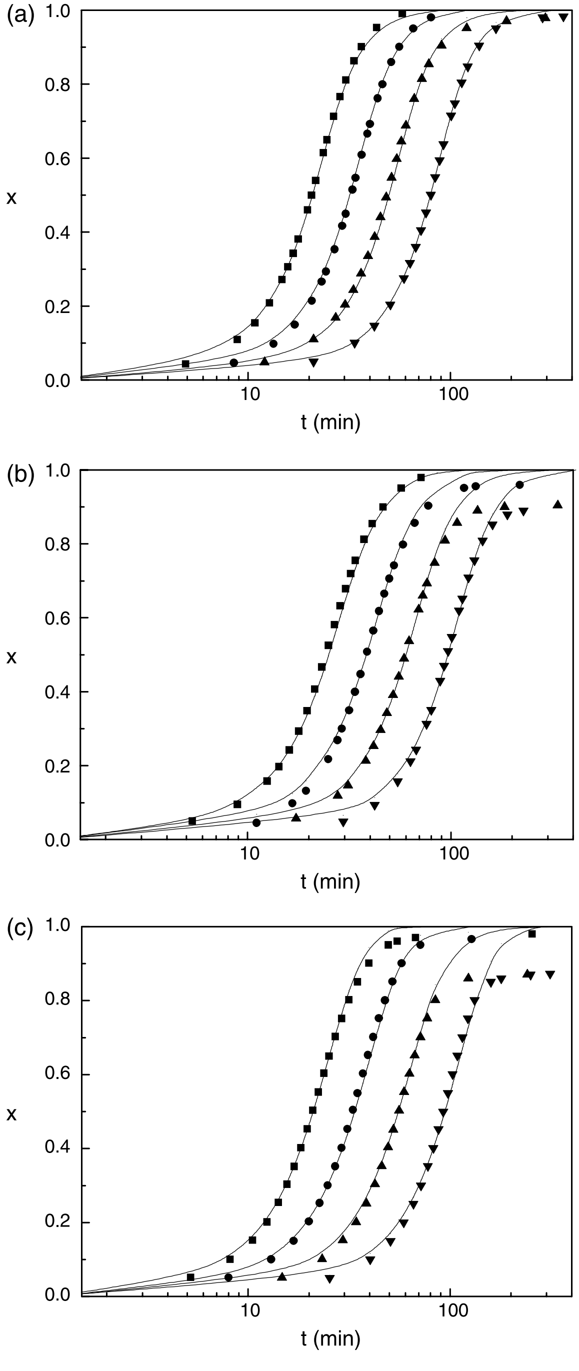


Fig. 7. Isothermal conversion versus time profiles for stoichiometric DGEBA/amine mixtures containing several *p*-toluidine:DDM ratios: (a) 1: 0.33, (b) 1:1, (c) 0.33:1. Temperatures employed are: (▼) 80 °C, (▲) 90 °C, (●) 100 °C, and (■) 110 °C. The solid lines represent the theoretical prediction of the mechanistic kinetic model.

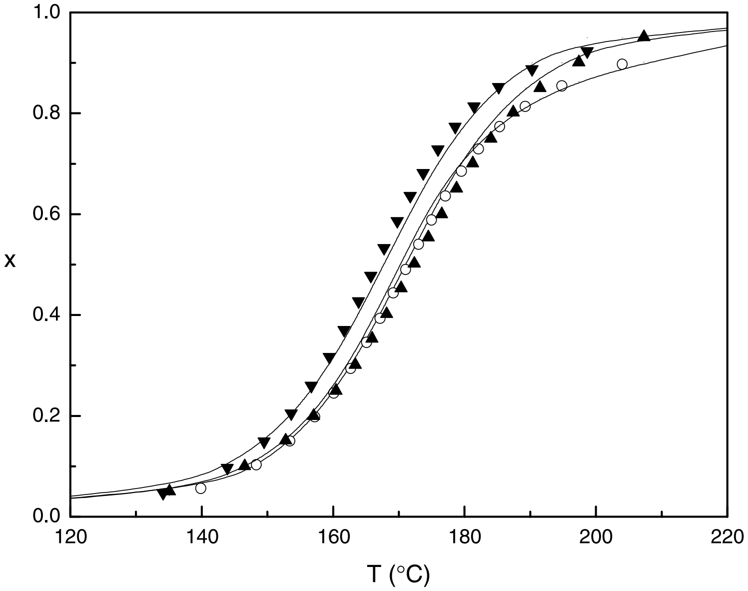


Fig. 8. Dynamic conversion versus temperature profiles for stoichiometric DGEBA/amine mixtures containing several *p*-toluidine:DDM ratios: (▲) 1:0.33, (○) 1:1, (▼) 0.33:1. The solid lines represent the theoretical prediction of the mechanistic kinetic model.

each step of the model. The change in the reaction medium has no significant influence on their values, as observed by Urbaczewski et al. [34]. Obtained kinetic rate parameters are summarized in Table 5. Values of dimensional addition constants of epoxy–primary amine, k_{1M}, k_{1D}, and complex–primary amine reactions, k'_{1M}, k'_{1D}, are very similar since the epoxy equivalents in these stoichiometric mixtures are approximately the same, independently of the proportion of monoamine and diamine employed.

The application of the proposed model to the mixtures of the monoamine and the diamine introduces more adjustable parameters, so it is interesting to show how the kinetic model fits the behaviour of mixtures with the rate constants found for the pure components, taking into account the different epoxy initial concentration and the mixture composition. In Figs. 9 and 10, the good agreement between predicted conversions and both isothermal and dynamic results for stoichiometric DGEBA/amine mixtures containing 1:1 *p*-toluidine:DDM ratio is shown. A similar agreement exists for the other mixtures.

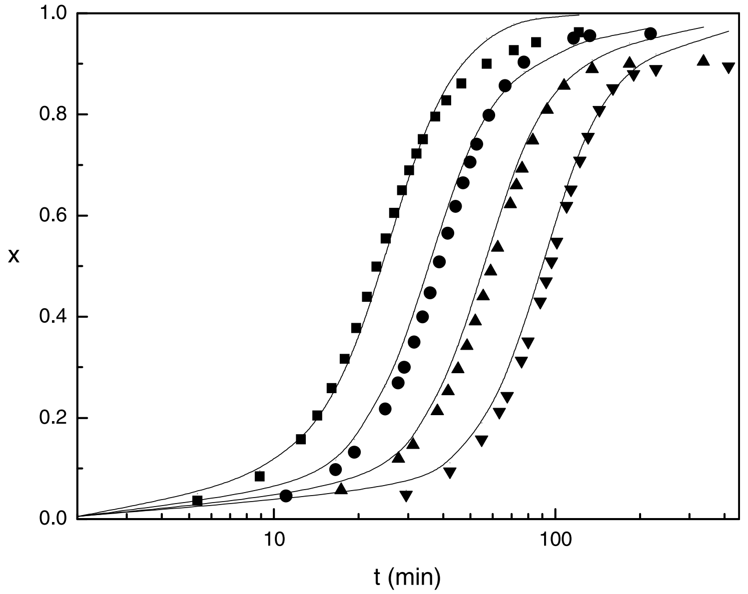


Fig. 9. Predicted isothermal conversion versus time profiles for stoichiometric DGEBA/amine mixture containing the 1:1 *p*-toluidine:DDM ratio, with the rate constants of the pure components. Temperatures employed are: (▼) 80 °C, (▲) 90 °C, (●) 100 °C, and (■) 110 °C. The solid lines represent the theoretical prediction of the mechanistic kinetic model.

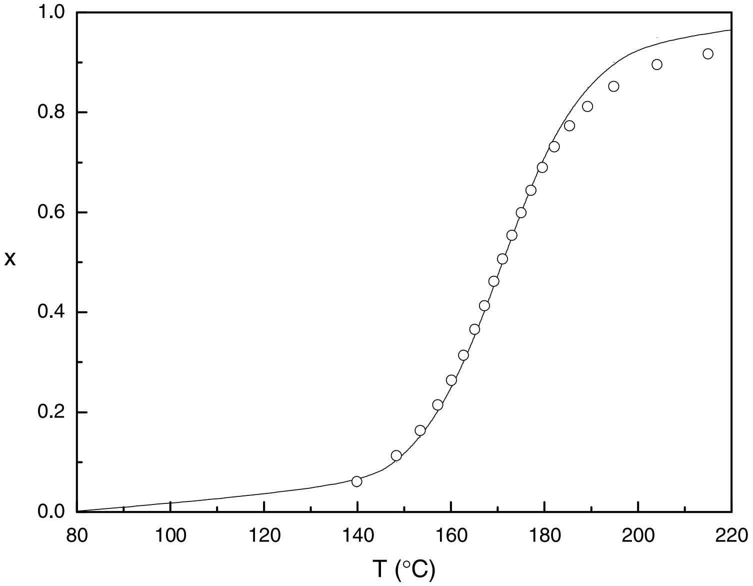


Fig. 10. Predicted dynamic conversion versus temperature profiles for stoichiometric DGEBA/amine mixtures containing the 1:1 *p*-toluidine:DDM ratio, with the rate constants of the pure components. The solid lines represent the theoretical prediction of the mechanistic kinetic model.

5. Conclusions

The polymerization kinetics of reactions between a monofunctional amine, a difunctional amine or a mixture of both with an epoxy prepolymer was analyzed using differential scanning calorimetry in both isothermal and dynamic conditions. A simple and reliable kinetic model of the consecutive and competitive reactions that take place during the polymerization has been employed to fit experimental results. The model includes an epoxy–hydroxyl complex as the only intermediate species and two possible mechanisms for the consumption of amine hydrogens, with free epoxy groups and with the epoxy–hydroxyl complex. During the formation of the epoxy–hydroxyl complex, the usually employed assumption (activation of the epoxide in a true equilibrium) has not been considered. The forward and backward reactions have been taking into account. The complex shows a Van't Hoff behaviour. An excellent fitting of the kinetic controlled region was obtained for all the amine mixtures employed with a lonely set of activation energies in isothermal and programmed heating-rate experiments. The presence of other types of equilibria, as proposed by others authors, can not be rejected but their consideration is unnecessary for the analysed systems.

Acknowledgements

M. Blanco wishes to thank University of the Basque Country (UPV/EHU) for her PhD grant. C. C. Riccardi grants Gobierno Vasco/Eusko Jaularitza for its financial support.

References

[1] Pascault JP, Sautereau H, Verdu J, Williams RJJ. Thermosetting polymers. New York: Marcel Dekker; 2002. p. 367–8 [chapter 12].
[2] Sindt O, Perez J, Gerard JF. Polymer 1996;37(14):2989–97.
[3] Lesser A, Crawford E. J Appl Polym Sci 1997;66(2):387–95.
[4] Crawford ED, Lesser AJ. J Polym Sci, Part B: Polym Phys 1998; 36(8):1371–82.
[5] Crawford ED, Lesser AJ. Polym Eng Sci 1999;39(2):385–92.
[6] Won YG, Galy J, Gerard JF, Pascault JP, Bellenger V, Verdu J. Polymer 1990;31(9):1787–92.
[7] Urbaczewski-Espuche E, Galy J, Gerard JF, Pascault JP, Sautereau H. Polym Eng Sci 1991;31(22):1572–80.
[8] Mayr AE, Cook WD, Edward GH. Polymer 1998;39(16):3719–24.
[9] Riccardi CC, Adabbo HE, Williams RJJ. J Polym Sci 1984;29(8): 2481–92.
[10] Chiao L. Macromolecules 1990;23(5):1286–90.
[11] Rozenberg BA. Adv Polym Sci 1985;75:113–65.
[12] Horie K, Hiura H, Sawada M, Mita I, Kambe H. J Polym Sci Part A-1 1970;8(6):1357–72.
[13] Swier S, Van Assche G, Van Mele B. J Appl Polym Sci 2004;91(5): 2798–813.
[14] Flammersheim HJ, Hörhold H, Bellstedt K, Klee J. Thermochim Acta 1985;92:185–8.
[15] Flammersheim HJ. Thermochim Acta 1998;310:153–9.
[16] Bonnet A, Pascault JP, Sautereau H, Taha M, Camberlin Y. Macromolecules 1999;32(25):8517–23.
[17] Riccardi CC, Williams RJJ. J Appl Polym Sci 1986;32(2):3445–56.
[18] Xu L, Schlup JR. J Appl Polym Sci 1998;67(5):895–901.
[19] Cole KC. Macromolecules 1991;24(11):3093–7.
[20] Smith IT. Polymer 1961;2:95–108.
[21] Riccardi CC, Fraga F, Dupuy J, Williams RJJ. J Appl Polym Sci 2001; 82(9):2319–25.
[22] Mijovic J, Fishbain A, Wijaya J. Macromolecules 1992;25(2):979–85.
[23] Mijovic J, Wijaya J. Macromolecules 1994;27(26):7589–600.
[24] Laidler KJ. Cinética de las reacciones: Reacciones en solución. vol. 1. Madrid: Alhambra; 1972. p. 49.
[25] Zucchi IA, Galante MJ, Borrajo J, Williams RJJ. Macromol Symp 2003;198:295–307.
[26] Flammersheim HJ. Thermochim Acta 1997;296:155–9.

[27] Girard-Reydet E, Riccardi CC, Sautereau H, Pascault JP. Macromolecules 1995;28(23):7599–607.

[28] Remiro PM, Riccardi CC, Corcuera MA, Mondragon I. J Appl Polym Sci 1999;74(4):772–80.

[29] Wise CW, Cook WD, Goodwin AA. Polymer 1997;38(13):3251–61.

[30] Swier S, Van Assche G, Van Mele B. J Appl Polym Sci 2004;91(5): 2814–33.

[31] Charlesworth JM. J Polym Sci, Part A: Polym Chem 1987;25: 731.

[32] Larrañaga M, Martin MD, Gabilondo N, Kortaberria G, Corcuera M A, Riccardi CC, et al. Polym Int 2004;53(10):1495–502.

[33] Flammersheim HJ, Opfermann J. Thermochim Acta 1999;337:141–8.

[34] Urbaczewski E, Pascault JP, Sautereau H, Riccardi CC, Moschiar SS, Williams RJJ. Makromol Chem 1990;191:943–53.