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Thermoplastic-modified epoxy resins cured with different functionalities amine mixtures. Kinetics and miscibility study

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Abstract The kinetics of a poly(methyl methacrylate) (PMMA)-modified epoxy resin cured with different functionalities amine mixtures was analyzed using differential scanning calorimetry (DSC) in both isothermal and dynamic conditions. A delay in the reaction rate was observed which increased with PMMA content. An approach of kinetic features involved in curing was carried out. A linear dependence of preexponential factors of neat systems with modifier content was considered. The approach shows the contribution of other factors including the dilution effect of the functional groups to the observed delay. Fourier transform infrared spectroscopy (FTIR) indicated a noticeable change in the interactions present in neat systems due to the presence of PMMA. On the other hand, a significant influence of the ratio between each amine in the epoxy/amine mixtures on the final physical appearance was observed. At constant curing conditions, materials from completely opaque (phase separated) to transparent (miscible) were obtained with the increase in monoamine content.

Keywords Differential scanning calorimetry · Functionality · Kinetics · Reaction-induced phase separation · Thermosets

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Introduction

Epoxy resins are reactive monomers, which are transformed by curing in thermoset polymers. Owing to their performance properties, they are extensively used in many applications. It is possible to tailor and improve polymer properties for specific applications, choosing between the wide variety of available curing agents and epoxy resins. The reactant functionality controls the development and the crosslink density of the network. When highly crosslinked networks are formed, due to their inherent brittleness some form of toughening is desirable [1–3]. The addition of initially miscible thermoplastics, which phase separate during matrix reaction, has been widely used to improve their fracture toughness, without a significant decrease of other desirable properties.

The ultimate morphology and behaviour of these blends are strongly dependent on the modifier chemical nature [4–6], the modifier content [7–9], the reactivity of the thermoset system and employed curing conditions [10–12]. Optimization of processing requires a reliable kinetic model. Kinetic mechanisms of epoxy resin curing have been intensively studied in the past applying different models, methods and experimental techniques [13, 14]. Nevertheless, curing of epoxy resins is quite complex, as many reactive processes occur simultaneously, which depend on the reactants employed and on their curing conditions. Apart from epoxy/amine addition reactions, secondary reactions can be necessary to be taken into account [15–18]. Other physical events such as gelation and vitrification phenomena, the phase separation process or the change from chemical to diffusion controlled kinetics during the reaction increase the complexity of curing process [19–21]. Furthermore, industrial epoxy/amine formulations are often composed of mixtures of some modifiers, epoxy and amine molecules, which can have different functionalities making more difficult the analysis.

For a better understanding of industrial formulation curing kinetics, the reaction of an epoxy resin previously mixed with several PMMA contents and cured with different functionalities amine mixtures was studied. Monoamine addition is the main novelty of the present work respect to those previously published about DGEBA/PMMA mixtures. Modifier content and amine ratio effects on reaction kinetics were analysed modifying the kinetic parameters obtained for neat epoxy/amine systems [22] taking into account the different concentration of initial epoxy groups and the mixture composition. The influence of hydrogen bonding formation between the components of these systems on cure kinetics was also analysed.

Experimental

A difunctional diglycidyl ether of bisphenol A (DGEBA), DER332, 4,4′-diaminodiphenylmethane (DDM) and *p*-toluidine were employed as resin, curing agent and chain extender, respectively. PMMA was employed as modifier. DGEBA and PMMA were placed in a vacuum oven at 80 °C overnight to remove any water present and amines were used as received without purification. Both amines had a similar chemical structure to ensure similar composition of the resultant products.

Modified mixtures were prepared by dissolving PMMA in dichloromethane and adding the resin with mechanical stirring. The resulting solutions were placed in an oil bath at 90 °C for several hours and thereafter, held overnight under vacuum at 90 °C. At this point, no phase separation was observed by differential scanning calorimetry (DSC) over the range 30–200 °C. Then, *p*-toluidine:DDM mixtures were added at 80 °C stirring vigorously for 5 min. Stoichiometric epoxy/amine equivalent ratio was used in all mixtures. Mixtures of amines were carried out at the following ratios of monoamine:diamine equivalents: 0:100, 25:75, 50:50, 75:25 and 100:0. Final amounts of PMMA in these matrices were 15, 20, 30 and 40 wt%. The corresponding neat matrices were also prepared by the same procedure.

DSC measurements were carried out in a Mettler Toledo DSC 821e module from −60 to 260 °C at 10 °C/min in a dry atmosphere with 5–10 mg samples. In a second dynamic scan the glass transition temperature of fully cured material, $T_{g\infty}$, was determined as the middle point of the endothermic shift. Kinetic study was also performed with isothermal scans at several temperatures. All samples were then cooled to room temperature and subjected to a dynamic scan from 30 to 260 °C at 10 °C/min to determine the residual enthalpy. Conversion was taken as the reaction enthalpy calculated from the isothermal scan at each time, divided by the total enthalpy obtained from the addition of the enthalpy from the isothermal mode to the residual one. Due to the high vapour pressure of *p*-toluidine, sealed aluminium pans were used [22]. The mixtures were poured into preheated moulds and cured for 5.5 h at 130 °C using vacuum during the first stages. Finally, they were postcured 2 h at $T_{g\infty}$+30 °C. The cured materials were analysed by Fourier transform infrared spectroscopy (FTIR) from 4,000 to 400 $\mathrm{cm^{-1}}$ in a Nicolet Nexus 670 spectrometer averaging 20 scans with 2 $\mathrm{cm^{-1}}$ resolution.

Results and discussion

The curing kinetics of PMMA modified epoxy/amine mixtures was studied by DSC in both dynamic and isothermal modes. All dynamic scans showed a step in the heat flow at low temperatures, due to glass transition from the glassy to the liquid state, T_{go}. An example is shown in Fig. 1. Positions of these transitions are reported in Table 1 along with those of polymerization peaks, T_{peak}, and the reaction enthalpies from dynamic scans, ΔH, for neat and modified mixtures. When PMMA was added, T_{go} was displaced to higher temperatures because of the miscibility of the higher T_g modifier with the epoxy precursor [10, 13–28]. On the other hand, an increase in the amount of *p*-toluidine resulted in the decrease of the initial T_{go} of all mixtures because the low molecular mass *p*-toluidine acted as a plasticizer. As temperature increased, epoxy/amine reaction transformed the initial mixture in a higher molecular mass system, thus giving rise to the exothermic peak. Major changes caused by the reaction in epoxy/monoamine systems were an increase in molecular mass and T_g which resulted in a linear structure. In systems with DDM and *p*-toluidine:DDM mixtures gelation and network formation occurred as well. Depending on the modifier content and on the ratio monoamine:diamine, phase separation could also occur during curing.

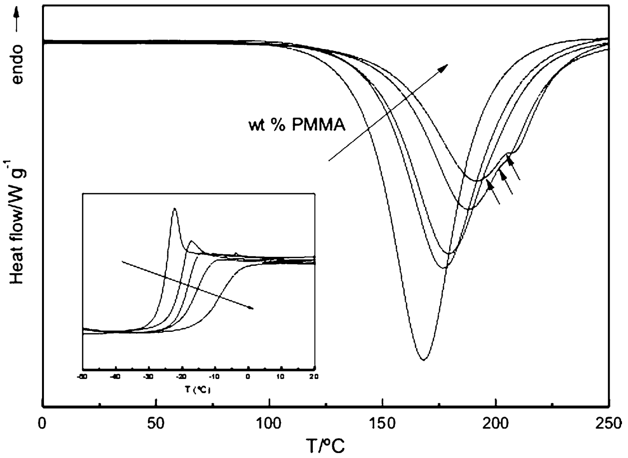

Fig. 1 Dynamic curves and details of T_{go} region for DGEBA/amine mixture containing *p*-toluidine:DDM ratio 25:75 modified with 0, 15, 20, 30 and 40 wt% PMMA

Table 1 Results of DSC dynamic scans of DGEBA/amine mixtures with different *p*-toluidine:DDM ratios modified with 0–40 wt% PMMA

p-Toluidine: DDM ratio	PMMA wt%	T_{go} (°C)	T_{peak} (°C)	$T_{shoulder}$ (°C)	ΔH (kJ/EE)	T_g epoxy (°C)	T_g PMMA (°C)
100:0	0	−42.0	173.0	–	102.5	92.0	–
	15	−36.0	181.0	–	97.5	88.5	–
	20	−33.0	181.0	–	94.5	88.5	–
	30	−28.5	190.0	–	86.5	89.0	–
	40	20.5	197.0	–	89.0	81.5	–
75:25	0	−35.0	172.0	–	105.0	108.0	–
	15	−32.0	179.0	–	103.0	101.0	–
	20	−28.5	180.5	–	103.0	98.0	–
	30	−24.0	190.5	–	86.0	98.0	–
	40	−18.0	196.0	–	85.5	91.0	–
50:50	0	−29.5	171.0	–	101.5	122.0	–
	15	−26.0	178.0	–	96.5	114.0	–
	20	−23.0	180.0	–	91.0	112.0	–
	30	−19.0	188.0	206.0	89.5	115.0	–
	40	−13.5	193.0	219.0	85.0	100.0	–
25:75	0	−24.0	168.0	–	100.0	137.0	–
	15	−19.5	177.0	–	100.0	132.0	–
	20	−18.0	180.0	195.0	96.0	134.5	115.0
	30	−15.0	188.0	202.0	91.5	137.0	106.5
	40	−9.5	191.5	204.5	93.0	114.0	103.5
0:100	0	−16.5	169.0	–	100.0	172.5	–
	15	−12.5	172.0	182.5	98.0	166.0	–
	20	−10.5	179.0	190.5	98.0	163.0	104.5
	30	−10.0	183.5	192.5	88.0	161.5	102.0
	40	−4.0	190.0	198.5	94.5	155.0	102.0

(–) Indicates that corresponding values are not observed by this technique

Exothermic reaction peaks were displaced to higher temperatures with PMMA addition. The clear delay in curing rate, also observed by others authors [18, 25, 27–32], mainly corresponds to physical reasons such as dilution effect and/or viscosity increase, but PMMA interactions with other groups present in the reaction medium could also contribute [29, 33]. For systems with higher PMMA contents, a shoulder appeared after the exothermic reaction peak. The absence of these shoulders in the neat system, along with the fact that its intensity increased with modifier content for every epoxy/amine systems, makes possible to ascribe them to an increase in the reaction rate of epoxy/amine-rich phase after modifier phase separation [18, 27, 29, 30]. Temperatures of shoulder appearance, $T_{shoulder}$, are also collected in Table 1. For constant PMMA content, an increase in the amount of monoamine resulted in the appearance of the shoulder at higher temperatures. The shoulder intensities decreased until its complete disappearance as monoamine content was higher, giving advice of the importance of the network formation in phase separation process.

ΔH values were in agreement with results reported in literature for neat systems [15, 33–35]. Mixtures with higher PMMA contents showed slightly lower values than corresponding ones for the employed amount of epoxy. In phase separated systems, some reactive groups could remain in PMMA-rich phase due to an incomplete phase separation process giving rise to a slight stoichiometric imbalance [10, 24, 25, 27, 36]. The difference was slightly higher with the increase in monoamine content. PMMA addition could hinder the reaction of all functional groups due to possible interactions between PMMA and other groups which could restrict the chain mobility. These possibilities could decrease the crosslinking density of the final matrices resulting in lower T_g values. In systems with higher monoamine contents, ΔH could be lower due to stronger interactions between PMMA and DGEBA/amine systems. Anyway, both similar curves and proximity of reaction heats for all mixtures indicated that similar chemical reactions occurred even though the polymerization rate was different. Hence, a common reaction mechanism can be used to describe the behaviour of all mixtures.

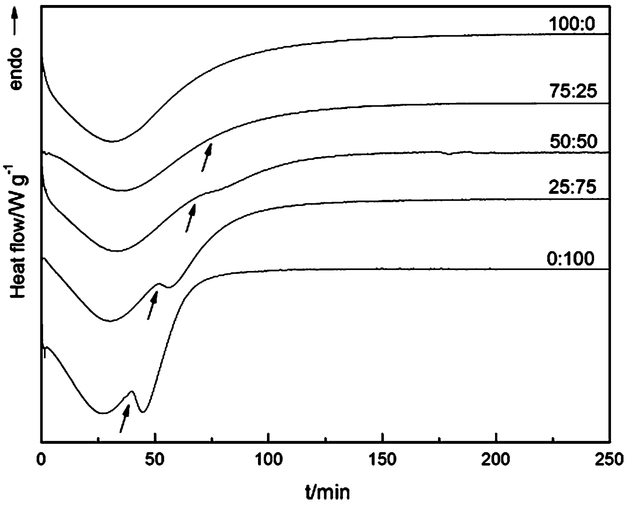

Fig. 2 Isothermal curves at 120 °C for DGEBA/amine mixtures modified with 40 wt% PMMA containing different *p*-toluidine:DDM ratios

Polymerization kinetics was also studied at different isothermal temperatures. In the same way than for previously reported DGEBA/DDM/PMMA system [10, 26, 27, 37], selected curing conditions and modifier contents have a great influence on kinetics and final appearance of cured samples for all *p*-toluidine:DDM ratios, since materials with different levels of miscibility were obtained. The influence of the change in monoamine content, which constitute the main novelty of this work, is shown in Fig. 2, where DSC curves obtained at 120 °C for mixtures with different *p*-toluidine:DDM ratios modified with 40 wt% PMMA are reported as an example. A similar delay was observed independently on the composition of the matrix. For systems with increasing DDM contents, a clearer shoulder emerged after the reaction peak. Times associated to shoulder appearance only provide a qualitative idea of the phase separation process, as the beginning of the process could be overlapped by the exothermal enthalpy. Figure 3 shows average conversion values at which shoulders appear ($x_{shoulder}$). The monoamine addition caused a delay in the shoulder appearance until $x_{shoulder}$ values close but slightly higher to the corresponding to gelation, pointing out the high miscibility of the modifier in the system. The conversion values associated to these shoulders are obtained from epoxy conversion profiles, shown in Fig. 4, obtained as explained in experimental section. Final conversions slightly increased because of the higher proximity between curing temperature and T_g values for the different systems. Full conversion was obtained in systems cured at temperatures higher than their $T_{g\infty}$. The shoulder intensities decreased with monoamine content. Apparently, monoamine acts as a compatibilizer of PMMA in mixtures cured with DDM, as can be corroborated from the final appearance of these systems, reported in a previous paper [38].

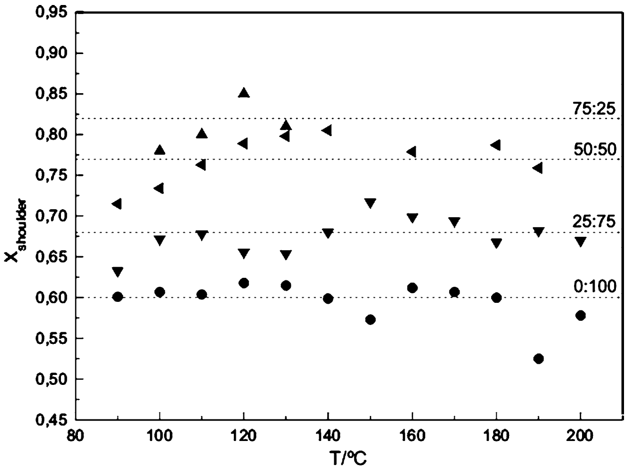

Fig. 3 Conversions corresponding to the appearance of the shoulder in DSC isothermal measurements for DGEBA/amine mixtures modified with 40 wt% PMMA containing *p*-toluidine:DDM ratios: (filled circle) 0:100, (filled inverted triangle) 25:75, (arrow head) 50:50 and (filled triangle) 75:25

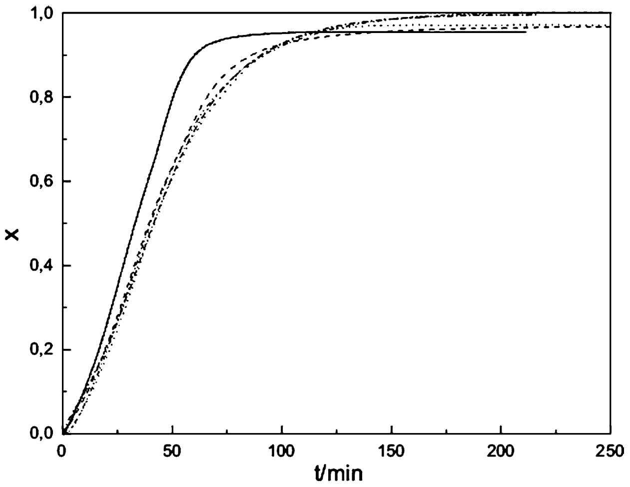

Fig. 4 Conversion profiles at 120 °C for DGEBA/amine mixtures modified with 40 wt% PMMA containing *p*-toluidine:DDM ratios: (—) 0:100, (– –) 25:75, (—) 50:50, (——) 75:25 and (— - -) 100:0

Besides the enthalpic contribution due to the change in the chemistry of the system during reaction, the entropic contribution to the free energy seems to be the main responsible for the differences found in the conversions associated to phase separation for the different mixtures, resulting values close to gelation values of each epoxy/amine system. As the chemical structure of epoxy/amine mixtures are quite similar for different *p*-toluidine:DDM ratios, the solubility parameters, δ (calculated by Fedor's molar group contribution [39] taking into account the amount of groups in the mixture), and thus their parameters should also be similar, as shown in Table 2 [40]. This fact corroborates the high entropic contribution to phase separation.

Table 2 Solubility parameters for epoxy/amine systems cured with different *p*-toluidine:DDM ratios

System	DGEBA	*p*-Toluidine	DDM	*p*-Toluidine:DDM ratio				
				0:100	25:75	50:50	75:25	100:0
δ (MPa)$^{0.5}$	20.2	19.9	21.8	21.0	20.9	20.8	20.6	20.5

Cure kinetics

Conversion versus time profiles showed a shape similar to that shown in Fig. 4 for all mixtures, which clearly evidenced the autocatalytic nature. In a previous paper [22], the obtained dynamic and isothermal results for neat systems were successfully fitted with a mechanistic kinetics model developed therein. The model, collected in Scheme 1, included an epoxy–hydroxyl complex as the only intermediate species and two mechanisms for the consumption of amine hydrogens, with free epoxy groups and with epoxy–hydroxyl complex. During the formation of epoxy–hydroxyl complex, the forward and backward reactions were taken into account, showing that E–OH complex possesses van't Hoff behaviour.

In the case of modified systems, the reaction kinetics can be simulated by supposing thermoplastic addition only leads to a dilution of reactive groups, so the rate constants of neat and modified systems must be the same [18, 24, 31]. This supposition predicts a faster reaction than the experimental results in both dynamic and isothermal modes. The difference between theoretical and experimental results increased with modifier content. Besides the dilution effect, other factors such as physico-chemical interactions between components could contribute to the delay in kinetics [27]. Figure 5 shows an example of obtained fitting.

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

$$\mathrm{E + A_1} \xrightarrow{k_1} \mathrm{A_2 + OH}$$

$$\mathrm{E + A_2} \xrightarrow{k_2} \mathrm{A_3 + OH}$$

$$\mathrm{E\text{-}OH + A_1} \xrightarrow{k'_1} \mathrm{A_2 + 2OH}$$

$$\mathrm{E\text{-}OH + A_2} \xrightarrow{k'_2} \mathrm{A_3 + 2OH}$$

Scheme 1 Epoxy/amine reaction scheme 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

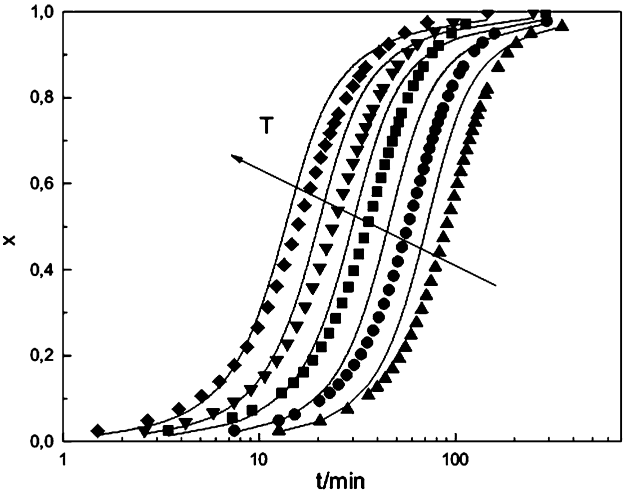

Fig. 5 Conversion profiles for DGEBA/amine mixture with *p*-toluidine:DDM ratio 75:25 modified with 20 wt% PMMA at temperatures from 90 to 120 °C. The solid lines represent the theoretical prediction taking into account the dilution effect

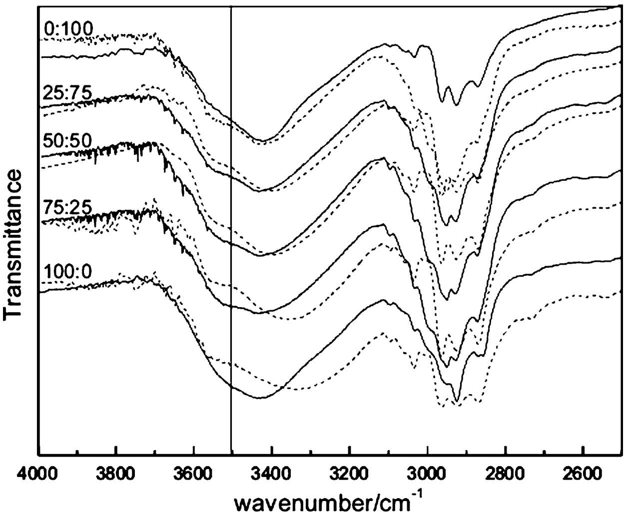

Fig. 6 FTIR spectra for cured (dashed lines) neat and (solid lines) 40 wt% PMMA modified systems and of cured DGEBA/amine mixtures containing different *p*-toluidine:DDM ratios

Interactions between PMMA and mixture components were analyzed by FTIR spectroscopy. Interactions between pure initial components are possible [25, 32, 38, 41, 42], but their characteristic bands did not show a clear shift to lower frequencies. Besides, fitting of experimental results, shown in Fig. 5, seems appropriate at low conversion values. On the other hand, –OH groups generated during epoxy/amine reactions are also capable of interact with other groups in the medium by hydrogen bonds. Figure 6 shows FTIR spectra of neat matrices and systems modified with 40% PMMA cured at 130 °C and postcured at $T_{g\infty} + 30$ °C. In neat systems, a band at approximately 3,555 cm^{-1} ascribed to the free –OH groups appeared [40], whereas associated –OH showed a wider and more intense band at lower frequencies. Spectra suffered a significant change with PMMA addition. PMMA could hinder or modify the hydrogen bonds in neat systems causing a redistribution of OH···N, OH···NH and OH···OH inter- and intramolecular interactions. In addition, –C=O groups of PMMA could also interact with generated –OH thus appearing a band centered around 3,500 cm^{-1} [43–45], which could be overlapped with the free –OH group band. PMMA caused more significant changes in hydrogen bonds of systems with higher monoamine contents pointing out stronger interactions, which could contribute to its higher miscibility in systems with higher monoamine contents. Moreover, they could justify the lower heat reaction values observed in dynamic DSC scans increasing monoamine content, as the interactions could hinder the chain mobility avoiding the full reaction of all functional groups.

The fail in the fitting of experimental results with the kinetic constants of neat systems modified taking into account only the dilution effect shows the necessity of a new mechanistic kinetics model including the influence of PMMA in the formation of complexes in the different epoxy/amine systems [46, 47]. Nevertheless, the inclusion of more complexes would lead to a high number of equations in the reaction scheme involving a great number of adjustable parameters and making its use unreliable under different experimental conditions [48]. So, taking into account that the kinetics predicted by this model described appropriately conversion shape and that the displacement between experimental and theoretical conversions was constant in each epoxy/amine system for every temperature, experimental results were fitted maintaining the same kinetic scheme but considering that preexponential factors are linearly dependent on modifier content. In this way, fitting of the results in DGEBA/DDM/PMMA mixtures was better than previously obtained applying other model [27].

Fitting considered that at the beginning of the reaction there was 0.015 equiv OH/equiv epoxy coming from epoxy molecule, maintaining the activation energy values found in neat systems in each step of the model. In spite of the different rate of reactions occurring in these systems, the same reactions occurred in neat and modified systems and the energy necessary for these reactions to take place should not

Table 3 Dimensional kinetic rate parameters obtained for epoxy/amine systems modified with 0–40 wt% PMMA

p-Toluidine: DDM ratio	PMMA wt%	$A_K\,(10^{-6})$ $\left(\frac{\text{L}}{\text{eq min}}\right)$	$A_{K'}\,(10^{-7})$ $\left(\frac{1}{\text{min}}\right)$	$A_{K_{1M}}\,(10^{-5})$ $\left(\frac{\text{L}}{\text{eq min}}\right)$	$A_{K'_{IM}}\,(10^{-4})$ $\left(\frac{\text{L}}{\text{eq min}}\right)$	$A_{K_{1D}}\,(10^{-5})$ $\left(\frac{\text{L}}{\text{eq min}}\right)$	$A_{K'_{1D}}\,(10^{-4})$ $\left(\frac{\text{L}}{\text{eq min}}\right)$
0:100	0	9.34	6.30	–	–	3.76	4.14
	15	7.26	6.09	–	–	7.23	3.94
	20	5.82	6.01	–	–	9.52	3.88
	30	4.18	5.82	–	–	10.4	3.71
	40	3.01	4.68	–	–	11.4	3.65
25:75	0	9.41	5.32	4.27	2.33	3.76	4.14
	15	5.41	5.11	5.30	2.11	7.82	3.70
	20	4.40	4.89	5.89	1.91	7.67	3.87
	30	3.02	4.83	7.34	1.81	7.69	3.73
	40	2.43	4.09	19.9	1.30	7.66	3.54
50:50	0	9.48	4.34	4.27	2.33	3.76	4.14
	15	5.20	4.12	5.08	2.05	7.93	3.89
	20	5.06	3.97	6.35	1.76	8.04	3.87
	30	4.32	3.85	27.4	1.39	6.54	3.80
	40	1.94	3.84	10.9	1.78	8.67	3.49
75:25	0	9.61	2.38	4.27	2.33	3.76	4.14
	15	5.99	3.13	5.48	2.13	6.57	3.57
	20	4.47	3.06	6.19	2.27	12.6	3.84
	30	3.81	2.88	4.79	1.66	9.88	3.67
	40	1.86	2.63	9.27	1.88	11.4	2.26
100:0	0	9.61	2.38	4.27	2.33	–	–
	15	5.10	2.13	6.03	2.10	–	–
	20	7.30	2.12	6.73	1.77	–	–
	30	3.47	1.96	5.90	2.01	–	–
	40	3.68	1.73	7.04	1.56	–	–

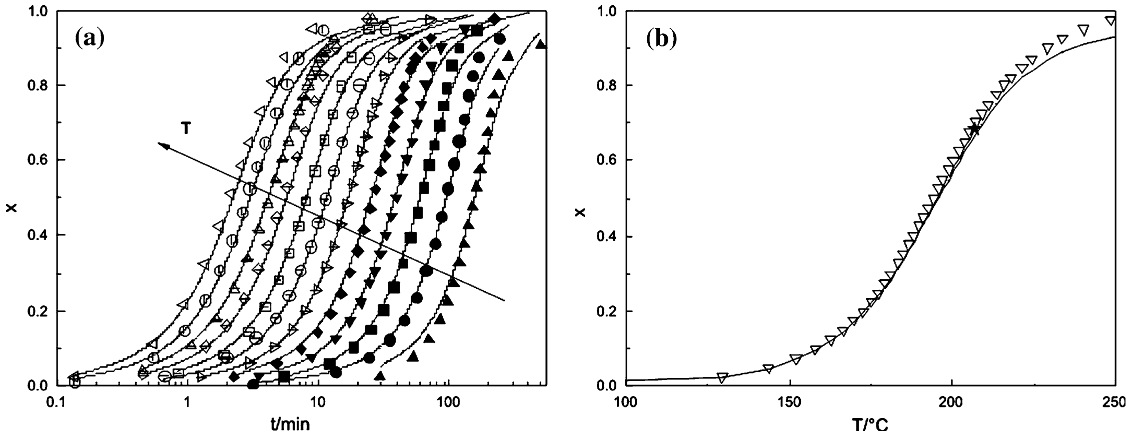

Fig. 7 Conversion profiles for DGEBA/amine mixtures containing *p*-toluidine:DDM ratio 25:75 modified with 40 wt% PMMA: **a** at temperatures from 90 to 200 °C, and **b** with dynamic scans. The solid lines represent the theoretical prediction with kinetic rate parameters in Table 1

be affected by the presence of the modifier. The change in the reaction medium has no significant influence on their values [49]. As reactivity of primary and secondary amine hydrogens was assumed independent on temperature and on the modifier presence, its values were considered constant and equal to 1 in monoamine [50, 51] and to 0.65 in diamine [27, 33, 52]. Dimensional kinetic parameters, summarized in Table 3, fitted satisfactorily the experimental results until phase separation [18] or gelation of the systems when these processes occurred [19–21]. As an example, Fig. 7a-b show, respectively, the fitting of isothermal and dynamic scans for the epoxy/amine system with *p*-toluidine:DDM ratio 25:75 modified with 40% PMMA. The slight deviation in isothermal experiments at high temperatures could be due to the presence of homopolymerization or etherification reactions of epoxy groups which were not taken into account in the reaction kinetics scheme [15–18]. The deviations found at high temperatures in dynamic scans, also observed in neat systems, can be ascribed to a change in the reaction mechanism due to the difficulty of forming the E–OH complex at high temperatures [48]. The values of the kinetic parameters indicate that the E–OH remained showing van't Hoff complex behaviour after the modifier addition, as previously shown in neat systems [22]. Rate constant for the reaction of E–OH with amine (k_1') is higher than that of the dissociation of the complex (k') [22].

Preexponential factors of the complex E–OH formation constant, A_K, decreased upon PMMA addition, as can be seen in Fig. 8. PMMA seems to hinder the formation of this complex by the dilution of the epoxy groups in the system or the possible formation of hydrogen bonds between carbonyl groups of PMMA and generated hydroxyl groups. After being formed, the complex E–OH could dissociate or react with amine groups. But, its global concentration in the reaction medium decreased with PMMA increase, as shown in Fig. 9 for the epoxy/amine system with *p*-toluidine:DDM

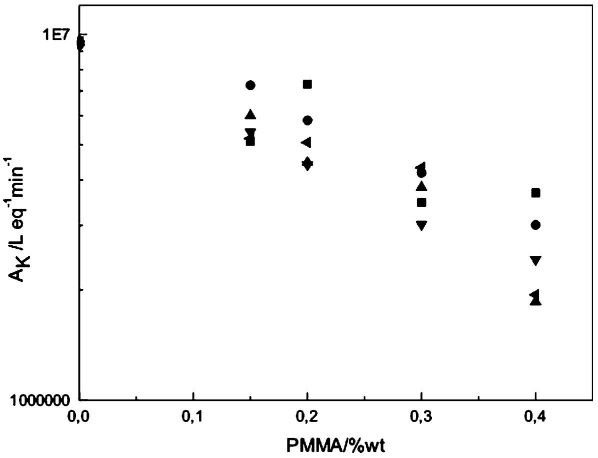

Fig. 8 Preexponential factors corresponding to DGEBA/amine mixtures containing *p*-toluidine:DDM ratios: (filled circle) 0:100, (filled inverted triangle) 25:75, (arrow head) 50:50 and (filled triangle) 75:25, (filled square) 100:0

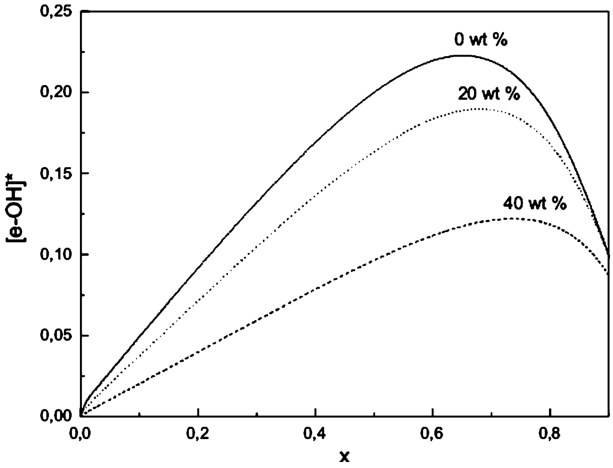

Fig. 9 Evolution of the E–OH complex concentration with conversion for DGEBA/amine mixtures containing *p*-toluidine:DDM ratio 50:50: (—) neat and modified with: (·····) 20 and (- - - -) 40 wt% PMMA

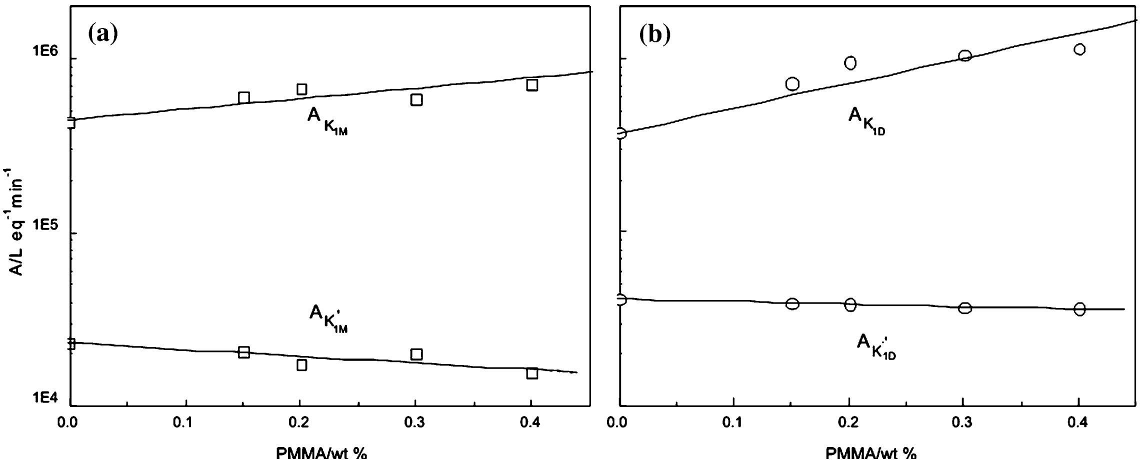

Fig. 10 Preexponential factors corresponding to epoxy/amine addition reaction catalyzed by the –OH groups and to the complex E–OH/amine reaction for: **a** DGEBA/*p*-toluidine, and **b** DGEBA/DDM mixtures

ratio 50:50. This decrease affected greatly kinetics, as E–OH complex is responsible for the autocatalytic behaviour of the reaction. Simultaneously, as less forming –OH groups existed interacting with epoxy groups when the content of modifier increased, more epoxy groups were available for direct reaction with amines [33]. Therefore, the addition constants corresponding to the reactions catalyzed by hydroxyl groups and impurities initially present in the formulation increased. On the other hand, values of addition constants for the epoxy–hydroxyl complex reaction with the amine hydrogens decreased slightly upon modifier addition. But these values remained approximately constant pointing out that after being formed the complex, its reaction rate did not change being the complex formation stage the responsible for the global reaction kinetics. This tendency is collected in Fig. 10a, b for DGEBA/monoamine and DGEBA/diamine modified systems in, respectively.

Conclusions

PMMA addition delays the reaction kinetics of an epoxy resin cured with different functionalities amine mixtures. The delay increases upon modifier content. Kinetic analysis shows that it is caused by physical reasons, dilution effect and/or viscosity increase, and also interactions between system components. PMMA hinders or modifies the hydrogen bonds of neat systems causing a redistribution of them through inter- and intramolecular interactions.

Fitting of experimental results with kinetic constants of neat systems modified considering a linear dependence of preexponential factors upon modifier content is suitable in the kinetic controlled region of all mixtures in dynamic and isothermal experiments until phase separation. The kinetic parameter analysis shows that E–OH complex in modified systems maintains a van't Hoff complex behaviour. PMMA hinders the E–OH complex formation, thus increasing the probability of direct epoxy/amine reactions. The kinetic parameter analysis shows that complex formation stage is the responsible for the global kinetics reaction.

The addition of monoamine delays to higher epoxy group conversions the phase separation process (when it occurs). Besides the enthalpic contribution due to the change in the chemistry of the system during reaction, the entropic contribution to the free energy seems to be the main responsible for the differences found in the conversions associated to phase separation for the different mixtures, resulting values close to gelation values of each epoxy/amine system. Physical interactions seem also to contribute to the higher miscibility of PMMA in the systems with higher monoamine contents and to the differences observed in the phase separation conversions, since interactions are stronger in these systems.

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