Cure Kinetics of Epoxy/Block-Copolymer Blends

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Abstract

This chapter deals with the study of the cure kinetics of epoxy/block copolymer blends in order to give a comprehensive account about the effect of adding this kind of modifier on the reaction rate of the network formation. Non-isothermal runs at constant heating rates and isothermal runs at constant temperature were carried out in order to determine the total heats of reaction released during curing for the epoxy blends modified with different contents of block copolymers. It was found a clearly delay of cure kinetics with the increase of block copolymer content. In order to understand the parameters affecting epoxy curing kinetics, the influence of block copolymer blocks chemical structure, and the molar ratio between blocks on the curing rate was also analyzed. Fourier transform infrared spectroscopy was used for this purpose. The experimental curves of isothermal curing were fitted to a phenomenological autocatalytic model and also to mechanistic model. Kinetics parameters were calculated from the previous models. The increase observed in activation energy values with the increase of block copolymer content corroborated that the physical interactions between the block copolymer and the epoxy significantly affect the curing behavior, agreeing with the observed delay.

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Introduction

During the curing process of a modified epoxy system, the cross-linking reactions involve a number of chemical and physical changes, while the material turns from a viscous liquid to a solid. The comprehension of the cure kinetic behavior related to the network formation permits a clear analysis of the structure/property/processing relationships that will determine the proper set of process parameters for the development of high-performance blends and composites with the best structural and morphological properties. Differential scanning calorimetry (DSC) has been widely employed to study the curing process of epoxy systems. This technique is very effective for monitoring the network formation since it permits the measurement of the amount of heat that is either absorbed or evolved during the course of polymerization reactions (i.e., epoxy–amine systems are well known as exothermic reactions). Several works have been published about DSC studies, both isothermal and non-isothermal heating mode, to determine the reaction rate curves and kinetic parameters for epoxy/amine systems (Grillet et al. 1989; Verchere et al. 1990; Cole 1991; Serier et al. 1991; Deng and Martin 1994; Girard-Reydet et al. 1995; Vyazovkin and Sbirrazzuoli 1996; Ghaemy and Khandani 1998; Karkanas and Partridge 2000; Vinnik and Roznyatovsky 2006) and theirs blends with thermoplastics (Bonnet et al. 1999; Varley et al. 2000; Bonnaud et al. 2000; Swier and Van Mele 2003a; Swier et al. 2005; Bejoy et al. 2006; Varley 2007; Zhang et al. 2009), rubbers (Kim and Kim 1994; Calabrese and Valenza 2003; Raju et al. 2007), and block copolymers (Swier and Van Mele 2003b, c; Larrañaga et al. 2004, 2005; Kim et al. 2005; Larrañaga et al. 2006a; George et al. 2012, 2014; Cano et al. 2014; Hu et al. 2015), among others.

Diverse mathematical models have been also applied in order to obtain a comprehensive description and simulation of the experimental cure profiles taking into account the catalytic effects and the influence of the diffusion phenomena. Modeling of the curing behavior of epoxy–amine systems can be approached both mechanistically (Mijovic et al. 1992; Mijovic and Wijaya 1994; Blanco et al. 2005; Zvetkov 2005) and phenomenologically (Ryan and Dutta 1979; Barton 1985; Roşu

et al. 2002; Du et al. 2004; Cai et al. 2008). Mechanistic models consider a complete scheme of consecutive and competitive reactions that take place during the curing process. As the cross-linking reaction of epoxy systems is very complex due to the close relationship between the chemical kinetics and changes in their physical properties, it is difficult to derive an accurate mechanistic model. Moreover, phenomena such as autocatalysis in the early stages or the effect of diffusion on the kinetic rate constants at later stages can further complicate modeling. Consequently, phenomenological approaches are preferred to study the curing kinetics of these thermosetting polymers. Phenomenological models are based on empirical or semi-empirical equations which explain the autocatalytic behavior of the epoxy–amine reaction. It should be pointed out that the unmodified epoxy–amine curing reaction is well known as an autocatalytic mechanism (Smith 1961; Riccardi et al. 1984; Xu et al. 1994). The autocatalysis in epoxy–amine reaction is attributed to a termolecular intermediate with hydroxyl groups produced during curing. On the other hand, the referred phenomenological models have been widely employed to study the cure kinetics because they are simple and fit experimental data with relative success.

The blending of an epoxy resin with block copolymers consisted of an epoxy phobic block and another epoxy phylic, and/or reactive blocks that are capable to control self-assembling at the nanometer scale in the uncured and cured state have been widely explored due to their excellent properties that can be tailored after the complete network formation, such as good mechanical behavior. As it is well known, the final self-assembled morphology of epoxy/block copolymer blends depends principally on both kinetics and thermodynamic factors, such as the curing rate, the change of the viscosity during the phase separation, as well as the modifier concentration, volume fraction of each block, architecture, and molecular weight of the blocks (Lipic et al. 1998; Girard-Reydet et al. 1999, 2002; Mijovic et al. 2000; Grubbs et al. 2000; Ritzenthaler et al. 2002, 2003, Rebizant et al. 2004; Dean et al. 2003; ; Serrano et al. 2005, 2006, 2007; Meng et al. 2006; Larrañaga et al. 2006a, b; Tercjak et al. 2006; Maiez-Tribut et al. 2007; Hermel-Davidock et al. 2007; Ruiz-Pérez et al. 2008; Liu et al. 2008, 2010; Ocando et al. 2008, 2013; Garate et al. 2011, 2013; Wu et al. 2013; Liu 2013; Xu et al. 2015).

In particular, the effect of blending an epoxy–amine system with different amounts of amphiphilic block copolymers, consisted on poly(ethylene oxide)-b-poly(propylene oxide)-b-poly(ethylene oxide) (PEP–PPO–PEO) with differing volume fractions of PEO block, on the cure kinetics during the network formation has been systematically studied (Larrañaga et al. 2004, 2005, 2006a). It is possible to point out that epoxy–amine systems blended with poly(ethylene oxide) homopolymer (PEO) lead to a miscible material owing to the fact that the OH groups, developed during the network formation of the growing epoxy matrix, interact by hydrogen bonding with the ether oxygen of PEO avoiding phase separation (Larrañaga et al. 2007), whereas the poly(propylene oxide) (PPO) tends to phase separate from the forming epoxy network as the molecular weight is increased by curing reaction. Nevertheless, as the miscibility between polymers is also governed

by the temperature of blending and composition, the control of both the reaction and the phase separation rate for a given modifier through the selection of an appropriate curing cycle (temperature vs. time) permits a fine-tune of the self-assembled morphologies (Liu 2013). Concerning this last argument, it was found that the phase separation in epoxy/PEO–PPO–PEO block copolymer blends at micro- or nanoscale depends mainly on the PEO content and curing temperature (Larrañaga et al. 2005). In addition, the cure kinetics curves obtained from DSC experiments of epoxy/PEP–PPO–PEO block copolymer blends were successfully fitted to an autocatalytic (Larrañaga et al. 2004) and mechanistic kinetic model (Larrañaga et al. 2005, 2006a). It was found that PEO–PPO–PEO slows the reaction rate both by acting as a diluent and by interfering with the autocatalytic process. This delay was related to a preferential hydrogen bonding interaction between the hydroxyl groups of the growing epoxy network and the PEO oxygens, which inhibit the autocatalysis process. Another finding was that the curing rate decreases with increasing block copolymer content in the epoxy blend as well as increasing PEO content in the block copolymer. This last fact also proved that the delaying of cure kinetics is mainly due to physical interactions between components (Larrañaga et al. 2006a).

Similar results about the delay on the cross-linking reaction of epoxy groups were obtained for epoxy/poly(styrene)-b-poly(ethylene oxide) (PS–PEO) block copolymer blends (Leonardi et al. 2015a). It is possible to emphasize that in these blends, the PS block was phase separated at low conversions, while the PEO block remained miscible up to very high conversions (Leonardi et al. 2015b). The lowering on reaction rate produced by block copolymer addition, illustrated in Fig. 1, was explained as a dilution effect by the large amount of miscible PEO block present in this copolymer as well as by a partial segregation of reactive monomers and short oligomers to the PS-rich phase. Regarding this last fact, it was established that a differential segregation of reactive components in both epoxy–amine-rich and block-rich phase can occur (Williams et al. 1997).

Interestingly, it was published a study about the cure kinetics of epoxy/poly (butadiene-co-acrylonitrile) (PS-PAN) blends. This study took into account the contribution of diffusion phenomena on the reaction rate after gelation and crosslinking of epoxy-amine systems in order to fit the experimental data near to vitrification using the autocatalytic model (Kim et al. 2005).

Finally, the kinetics of curing of an epoxy system and their blends with epoxidized poly(styrene)-b-poly(butadiene)-b-poly(styrene) (eSBS) was studied using isothermal and non-isothermal DSC analyses (George et al. 2012, 2014). The experimental cure kinetics curves were phenomenologically modeled with success. It is possible to emphasize that the eSBS used for this study was a block copolymer with high degree of epoxidation (eSBS 47 mol%) to ensure the nanostructuring of these blends (Ocando et al. 2008).

The most relevant results about the effect of block copolymer addition on cure behavior of epoxy–amine blends by DSC analyses, as well as a comprehensive understanding of the kinetic parameters by applying mathematical models to describe the obtained experimental data, will be addressed in this chapter.

Fig. 1 Conversion of epoxy groups at 135 °C for blends containing 0, 40, and 60 wt% BCP (Reprinted with permission Leonardi et al. (2015a))
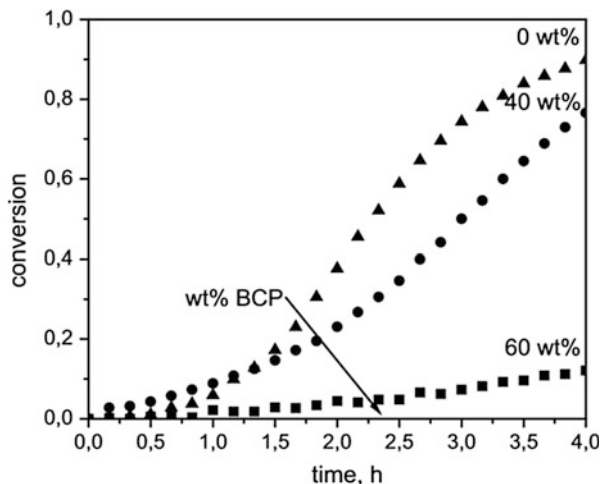
Non-isothermal DSC Analyses

In general, the heat released during the network formation determined by non-isothermal or dynamic DSC measurements is assumed to be directly proportional to the extent of consumption of the reactive groups in epoxy–amine systems. Non-isothermal runs at constant heating rates were carried out in order to determine the total heats of reaction (ΔH_T) released during dynamic curing for the epoxy blends modified with 10, 20, and 30 wt% of PEO–PPO–PEO (EP) block copolymer ($M_{EO} = 1088$ and $M_{PO} = 1794$ g mol^{-1}) with a molar ratio between blocks, PEO: PPO, of 0.8:1 (EP-0.8:1) (Larrañaga et al. 2004). The epoxy–amine system used for this study was a diglycidylether of bisphenol A (DGEBA)/4,4-diaminodiphenylmethane (DDM) system. From the dynamic curing profiles (Fig. 2), it was concluded that the curing reaction for the studied systems was kinetically affected by the modifier content. This fact was proved by a displacement of exothermic polymerization temperature peaks (T_p) to higher values as the concentration of block copolymer in the blend increases. Regarding the ΔH_T, it was observed that the presence of block copolymer did not affect the reaction pathway due to this value decrease in proportion to the block copolymer content in the blend (Table 1). In addition, as can be seen from dynamic curing profiles (Fig. 2), a shoulder appeared (T_{sh}) after the exothermic polymerization peak for the epoxy blends. This last behavior was attributed to the phase separation of the block copolymer, and it was corroborated by light transmission dynamic scan by the same authors. Table 1 summarizes the obtained values of ΔH_T, T_p, and T_{sh} determined by DSC as well as the cloud point temperature (T_{cp}) determined by transmission optical microscopy (TOM), a temperature where the phase separation occurs, and it was in agreement with T_{sh}.

Fig. 2 DSC dynamic scans
carried out at a rate of
$10\,°C\,min^{-1}$, for epoxy
mixtures containing various
PEO-PPO-PEO contents
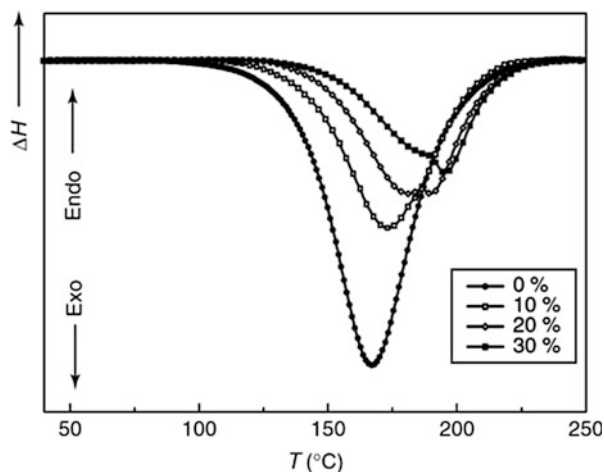(Reprinted with permission
Larrañaga et al. (2004))

Table 1 Thermal properties and TOM measurements of the PEO–PPO–PEO-modified epoxy
mixtures (Reprinted with permission Larrañaga et al. (2004))

PEO–PPO–PEO content (wt%)	H_T (kJ (epoxy equivalent)$^{-1}$)	T_p (°C)	T_{cp} (°C)	T_{sh} (°C)
0	101	171	–	–
10	87	174	173	180
20	75	179	180	184
30	65	185	187	188

The observed delaying behavior on curing reaction was related to dilution effects, due to a reduction in the density of the reactive groups as the block copolymer content increased. Nevertheless, the authors also pointed out that in this epoxy/ PEO–PPO–PEO blend, the delay on curing reaction was higher than the one observed in other epoxy blends containing other modifiers (Jenninger et al. 2000). Therefore, this observed behavior could not be explained only by a dilution effect. This fact suggested that the OH groups (developed in the cure reactions) interact through hydrogen bonding with ether oxygen of PEO, so decreasing the autocatalytic process, and therefore delaying the curing process (Larrañaga et al. 2007). Fourier transform infrared spectroscopy (FTIR) analyses (Fig. 3a) confirmed this hypothesis, revealing that the associated hydroxyl group bands shifted to lower wave numbers. In addition, from Fig. 3b, it was noticed that the intensity ratio between the associated hydroxyl band and the free hydroxyl band around $3570\,cm^{-1}$ in the modified system increased with the increment of the conversion, and this increment is more significant compared with the unmodified systems (Larrañaga et al. 2004).

The influence on the delaying of cure rate with the molar ratio between blocks of diverse PEO–PPO–PEO (EP-0.33:1, EP-0.8:1, and EP-3:1) block copolymers was also demonstrated by DSC analyses (Larrañaga et al. 2006a). Figure 4b shows the
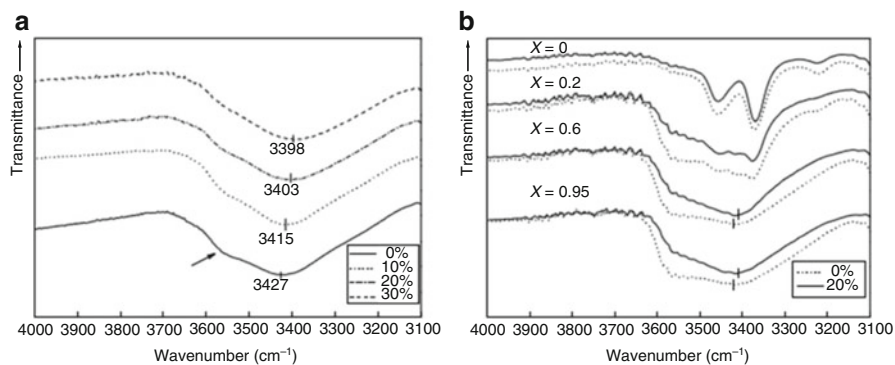
Fig. 3 FTIR spectra for (**a**) all cured samples with various contents of modifier and (**b**) for neat epoxy and a 20 wt% PEO-PPO-PEO-modified mixture at different conversions (Reprinted with permission Larrañaga et al. (2004))

Fig. 4 DSC dynamic scans for (**a**) epoxy systems with various EP-0.33:1 contents and (**b**) neat epoxy and 30 wt% PEO-PPO-PEO-modified systems (Reprinted with permission Larrañaga et al. (2006a))
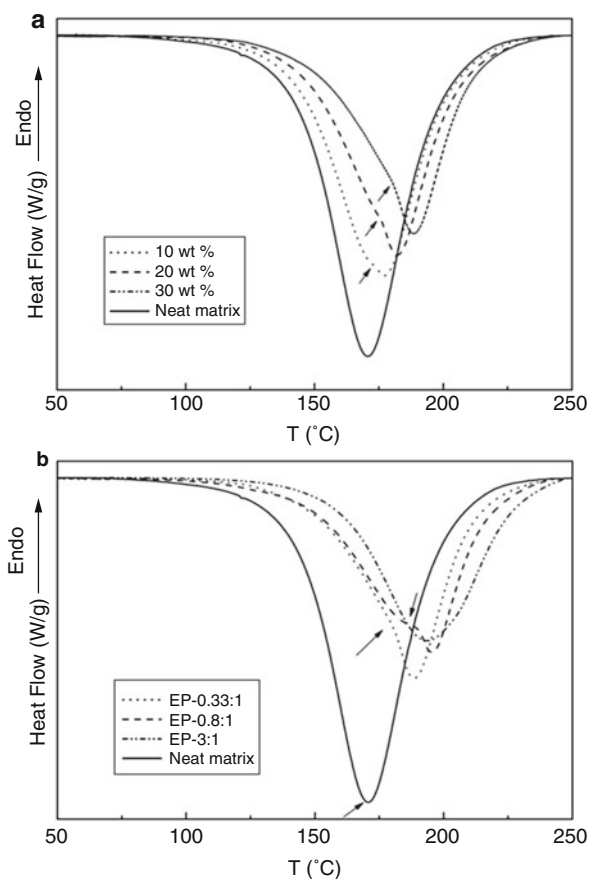
Table 2 Heat of reaction and T_{peak} values of neat epoxy and with various contents of eSBS (Reprinted with permission George et al. (2012))

wt% of eSBS in DGEBA/ eSBS(47 mol%)/DDM	Heating rate (°C min^{-1})	ΔH_0 (J/g)	T_{peak}(°C)
0	2.5	558.7	128.3
	5	534.6	143.8
	7.5	485.8	154.8
	10	470.8	162.1
10	2.5	575.2	130.6
	5	526.1	148.4
	7.5	454.2	160.0
	10	449.6	166.4
20	2.5	532.5	129.8
	5	496.7	147.7
	7.5	455.7	163.1
	10	434.6	170.5
30	2.5	488.5	138.2
	5	485.1	153.4
	7.5	434.6	163.4
	10	364.8	171.1

dynamic thermograms for a neat epoxy–amine system and its blends containing 30 wt% of EP-0.33:1, EP-0.8:1, and EP-3:1. It was found that the displacement of exothermic peak was higher for the modified epoxy blend with high PEO content. This behavior was attributed to the occurrence of more physical interactions between the epoxy and PEO block in the blend modified with EP-3:1. The occurrence of more physical interactions was also confirmed by FTIR analyses. In addition, the shoulder in the dynamic heating profiles attributed to the macrophase separation process was observed in EP-0.33:1 and EP-0.8:1 modified epoxy blends but not for the block copolymer with high PEO content.

A recent work was published about the effect of the addition of different amounts of eSBS block copolymer with 47 mol% of polybutadiene block epoxidation (eSBS47) on the cure kinetics of epoxy blends (George et al. 2012). The epoxy–amine system used in this study was DGEBA/DDM. Dynamic DSC experiments were carried out at different heating rates for the epoxy systems modified with 0, 10, 20, and 30 wt% of eSBS. It was observed that the exothermic peak maximum (T_{peak}) undergoes a displacement to higher temperatures when heating rate was increased. This behavior was also observed at different blend composition. The average of enthalpy values obtained at different heating rate was used to estimate the total heat of the reaction (Table 2). From these results, it was noticed that the minimum in the exothermic curve corresponding to the maximum heat flow of the epoxy–amine reaction increases as the weight percentage of eSBS in the epoxy blend increases. This behavior was related to a plasticization effect and interactions between the epoxidized PB segments with the epoxy resin that causes retardation
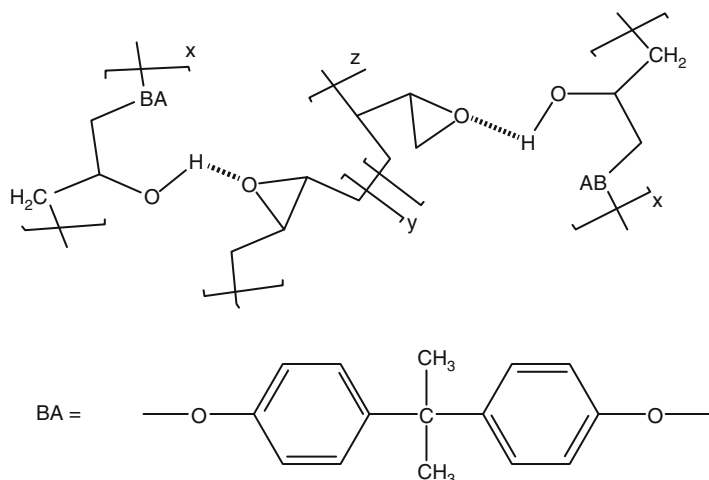
Fig. 5 Schematic representation of hydrogen bonding interaction between hydroxyl hydrogen in DGEBA and epoxy oxygen atom of epoxidized SBS (1,4- and 1,2-epoxidized PB) (Reprinted with permission George et al. (2012))

in cure reaction. FTIR studies carried out by the same authors corroborated the presence of interactions between the hydroxyl group of the growing epoxy network and oxirane groups of the epoxidized polybutadiene. The schematic representation of hydrogen bonding interaction between the epoxy resin and eSBS is illustrated in Fig. 5.

In a subsequent work, the same authors studied the evolution of the total heats of reaction of an epoxy blend modified with 10 wt% of eSBS47 at different cure times by dynamic DSC measurements. For the kinetic studies, the epoxy blends were cured in an air oven for different periods at 90 °C prior to DSC analyses. From this study, it was observed that the evolution of the total heats of reaction for the 10 wt% eSBS47-modified epoxy blend decreased as a function of cure time, as a result of the epoxy–amine reaction, and essentially no exothermic reaction was observed when the cure time reached 90 min. This behavior was related to the fact that the mobility of some reactive sites could be frozen, causing an ending of the polymerization (George et al. 2014).

Interestingly, a recent study about the curing behavior of a cyanate ester/epoxy system and its blends containing PEO–PPO–PEO with molecular weight Mw = 8600 (F68) was published (Hu et al. 2015). For this purpose, the authors developed a series of mixtures varying the matrix composition (cyanate ester/epoxy ratio) and the block copolymer contents (up to 20 wt%). The matrix composition was varied, and some differences about the hydrogen bonding interactions and chemical reaction resulting from the cross-linked network structures were observed. DSC analyses (Fig. 6) revealed an exothermic polymerization peak at lower temperature that was related to homopolymerization reactions of cyanate ester groups. On the other hand,
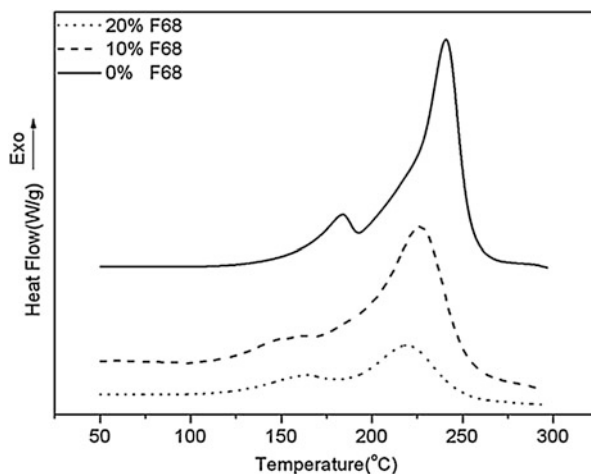
the exothermic polymerization peak observed at higher temperature was related to the formation of oxazolidinone groups (reaction between epoxy–cyanate ester). On the contrary to the results described above, this study indicated that cure reaction was accelerated by the incorporation of a small amount of block copolymer. In addition, the exothermic polymerization peak at lower temperature was less notorious in the case of higher block copolymer contents. Therefore, it was concluded that the presence of hydroxyl groups in block copolymers had a significant catalytic effect on the curing of cyanate ester/epoxy resins. This catalytic behavior was also corroborated by FTIR analyses, where it was clearly observed that the disappearing rate of both cyanate and epoxy groups was faster for the modified system than that of the neat resin.

Isothermal DSC Analyses

The curing rate of different contents of PEO–PPO–PEO block copolymer with 30wt% of PEO (EPE) blended with a DGEBA/m-xylylenediamine system was studied using DSC under isothermal conditions (Cano et al. 2014). The curing temperature for this purpose was chosen taking into account the lower critical solution temperature (LCST) behavior of this block copolymer. In this sense, isothermal runs at 25 °C were performed to the epoxy blends, and the resulting thermograms are shown in Fig. 7. The curing reaction between the epoxy resin and the amine was indicated as the drop in heat flow, and the reaction was considered complete when the isothermal DSC traces leveled off to the baseline. In agreement with the non-isothermal studies previously shown in this chapter, from these results, a clear delay in the curing reaction with the increment of the block copolymer content was also found. This behavior on curing reaction time was again related to the dilution effect in the blends that makes the reaction between the epoxy and the amine groups more difficult.
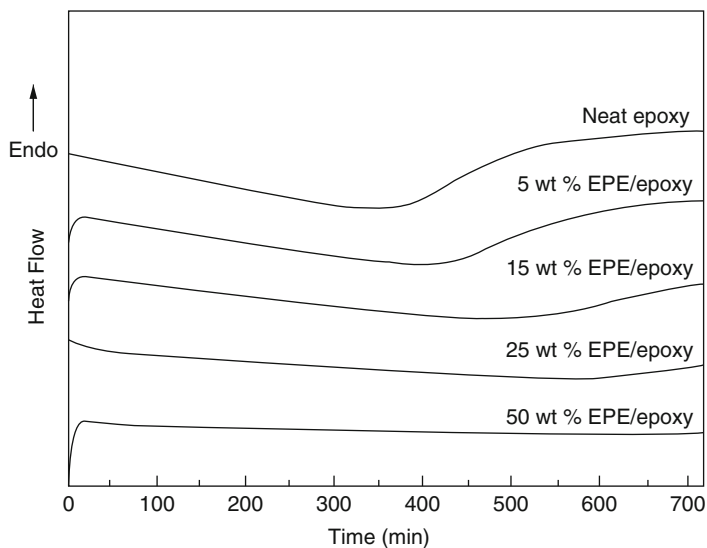
Fig. 7 Isothermal DSC thermograms of the neat epoxy system and all EPE/epoxy systems at 25 °C (Reprinted with permission Cano et al. (2014))

In addition, it was also pointed out that the presence of more physical interactions between the epoxy resin and the PEO–PPO–PEO block copolymer by an increment on the amount of modifier, from 5 to 50 wt%, can be also responsible for the delay on curing rate.

Similar results about the curing rate of epoxy blends depending on the amount of PEO–PPO–PEO block copolymer were obtained at an isothermal cure temperature of 120 °C (Larrañaga et al. 2004). It was observed from the reaction rate curves (dX/dt vs. time) that the peak for the maximum reaction rate decreased and the time at which this maximum takes places increase with the block copolymer content (Fig. 8). In addition, the authors related the shoulder observed in the reaction rate trace of the modified system with 30 wt% block copolymer with the occurrence of a macroseparation at the curing temperature of 120 °C. This last behavior was corroborated by the measurement of the cloud point by light transmission analysis at 120 °C.

Interestingly, the influence of the curing temperature and block copolymer content on cure kinetics of epoxy/PEO–PPO–PEO block copolymer blends analyzed by isothermal DSC experiments was correctly fitted to a phenomenological autocatalytic model assuming equal reactivity of primary and secondary amino hydrogens with the epoxy groups (Larrañaga et al. 2004). The epoxy–amine system used for this study was a diglycidylether of bisphenol A (DGEBA)/4,4-diaminodiphenylmethane (DDM) system. This phenomenological autocatalytic approach employs empirical or semiempirical equations (Kamal and Sourour 1973; Sourour and Kamal 1976). Explained in a more detailed way, this model takes into account the reactions of the oxirane groups with the primary and

Fig. 8 Reaction rate curves
of the epoxy mixtures
containing various amounts of
block copolymer cured at
120 °C (Reprinted with
permission Larrañaga
et al. (2004))
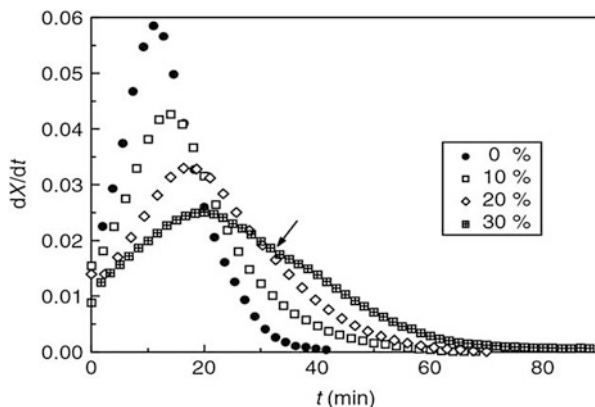
secondary amines, as well as catalytic and autocatalytic effects. The generalized
equation for this autocatalytic model is described by (Eq. 1):

$$\frac{dX}{dt} = (k_1 + k_2 X^m)(1 - X)^n \tag{1}$$

where k_1 and k_2 correspond to the rate constant for the reaction catalyzed by proton
donors initially present in the system (e.g., α-glycols present in the epoxy monomer)
and proton donors that are produced during cure, respectively; X denotes the
conversion of the epoxy groups, m and n are the kinetic exponents of the reactions,
and $m + n$ is the overall reaction order. The rate constants k_1 and k_2 are dependent on
the temperature with an Arrhenius-type relationship: $k_1 = A_1 \exp(-E_{a1}/RT)$ and $k_2
= A_2 \exp(E_{a2}/RT)$, where A_i denotes the collision frequency or Arrhenius frequency
factor, E_{ai} its corresponding activation energy, R the gas constant, and T the absolute
temperature. In order to obtain accurate values of Eq. 1 parameters from isothermal
curve data, a simple iterative method can be utilized until an apparent convergence of
the m and n values is obtained, and Eq. 1 can be rewritten as

$$ln\left(\frac{dX}{dt}\right) - ln(k_1 + k_2 X^m) = n\,ln(1 - X) \tag{2}$$

This equation takes into account the autocatalytic nature of the curing process with
the term $k_2 X^m$, while the uncatalyzed process is represented by k_1. The values of E_{a1}
and E_{a2} were obtained by plotting $\ln k_1$ and $\ln k_2$, respectively, versus $1/T$. Therefore,
Arrhenius plots of the rate constants from isothermal runs were characterized for
straight lines where the slope is E_{a1}/RT and E_{a2}/RT and the intercept is $\ln A_1$ and $\ln A_2$,
respectively. The summarized kinetics parameters, reaction constants, and activation
energy, obtained for the epoxy/PEO–PPO–PEO blends, are shown in Table 3. From
these results, it was pointed out that the reaction orders did not change very much
with the content of block copolymer in the blend as well as with the cure

Table 3 Kinetic constants obtained for the PEO–PPO–PEO-modified epoxy mixtures (Reprinted with permission Larrañaga et al. (2004))

PEO–PPO–PEO content (wt%)	T_{cure} (°C)	m	n	$k_1 \times 10^3$ (min^{-1})	$k_2 \times 10^3$ (min^{-1})	E_{a1} (kJ mol^{-1})	E_{a2} (kJ mol^{-1})	$\ln A_1$	$\ln A_2$
	80	0.98	1.11	1.5	45.6				
	100	0.97	1.12	5.1	107.7				
0	120	0.95	1.18	11.0	198.5	57.9	44.6	13.29	12.16
	140	0.93	1.22	28.0	427.4				
	80	0.99	1.40	1.4	37.0				
	100	0.97	1.42	4.9	85.0				
10	120	0.93	1.39	10.5	174.2	58.5	44	13.41	11.71
	140	0.93	1.37	26.0	326.8				
	80	0.91	1.37	1.3	28.6				
	100	0.91	1.29	4.5	56.8				
20	120	0.97	1.26	10.0	126.6	58.6	44.4	13.38	11.51
	140	0.91	1.35	25.0	246.2				
	80	0.93	1.23	1.1	19.4				
	100	0.91	1.22	4.2	39.1				
30	120	0.87	1.25	9.5	82.5	58.8	42.7	13.33	10.58
	140	0.81	1.34	21.0	158.6				

Fig. 9 Comparisons between
the autocatalytic model and
experimental data for the
mixture modified with a
20 wt% block copolymer at
various cure temperatures
(Reprinted with permission
Larrañaga et al. (2004))
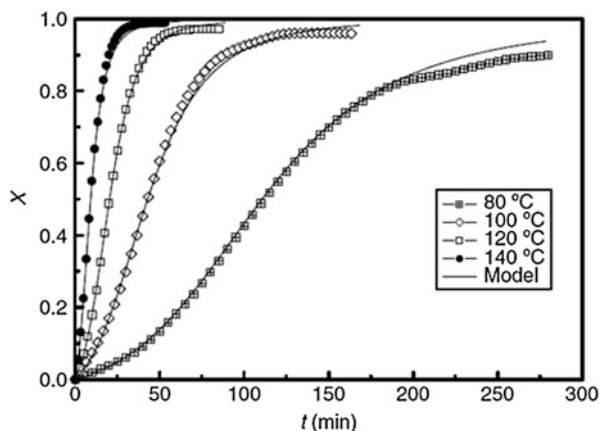
temperature. On the other hand, k_2 decreased at all temperatures as the block copolymer content increases. This reduction in k_2 was related to the decrease in the autocatalytic effect by specific interactions between the hydroxyl groups and the block copolymer. As discussed before these interactions were demonstrated by FTIR analyses (Fig. 3).

Figure 9 presents a comparison between the autocatalytic model and the experimental data for epoxy blends modified with 20 wt% of PEO–PPO–PEO. It is possible to emphasize that the experimental conversion values at a given temperature were defined as the ratio between the enthalpy of reaction at time t, $(\Delta H_{iso})_t$, and the sum of the total enthalpy from the isothermal and residual scans $((\Delta H_{iso}) + (\Delta H_{res}))$. As can be seen, the model fitted quite well with the experimental conversion curves; small variations between experimental and theoretical values were related to vitrification effects (Larrañaga et al. 2004). Similar results about cure kinetics studies of epoxy blends, by the use of isothermal DSC analyses and a modified autocatalytic kinetic model, were obtained for the same group when an epoxy resin was modified with different amounts of two kinds of thermoplastics polymers (Fernández et al. 2001). It is possible to point out that the conversion increases in the initial stages of reaction, and then the cure reaction rate decreases at later stages because the blends became vitrified. This decrease in the cure reaction rate is related to the cross-linking density. In addition, the maximum in reaction rate against time plot is typical of autocatalytic mechanism. Therefore, it was concluded that the presence of block copolymer in the epoxy blends does not affect the autocatalytic nature of the reaction.

In a later work, the same authors (Larrañaga et al. 2005) used a mechanistic model to fit the experimental results obtained by DSC for the DGEBA/DDM system modified with PEO–PPO–PEO block copolymer. The employed

mechanistic kinetic model considers a scheme of consecutive and competitive reactions that can take place during the curing process (Riccardi et al. 2001). As mentioned before, the curing process of epoxy–amine systems is a very complex procedure due to the chemical reactions and changes in the physical properties which are closely related; in this sense it is difficult to obtain an accurate mechanistic model (Riccardi and Williams 1986a, b; Mijovic et al. 1992; Mijovic and Wijaya 1994; Urbaczewski et al. 1990; Blanco et al. 2005; Zvetkov 2005). Nevertheless, Riccardi et al. (2001) introduced a simple mechanistic model that encloses an equilibrium reaction that produces an epoxy–hydroxyl complex established as the only intermediate species as well as two possible mechanisms for the use of amine hydrogens. It was found that this simple mechanism model provided a good fitting with respect to the experimental results obtained by DSC for the DGEBA/ethylenediamine (EDA) system, under both isothermal and constant heating rate conditions. It is possible to emphasize that the main advantage of this mechanistic model with respect to the phenomenological model is that the mechanistic model offers more predictive capability due to the results obtained from its equations which can be extrapolated to account for variations in the initial formulations (Chiao 1990; Chiao and Lyon 1990). In addition, this model can give an insight about the network structure. As a result, the evolution of different statistical parameters during the network formation can be predicted (Riccardi and Williams 1986b).

In this sense, following the work presented by Riccardi et al. about epoxy–amine systems (Riccardi et al. 2001), Larrañaga et al. proposed a mechanistic approach that includes the following alternatives for the curing reaction steps (Larrañaga et al. 2005): (1) epoxy activation by hydrogen bonding with hydroxyl groups in the pre-equilibrium to form an epoxy–hydroxyl complex, (2) uncatalyzed addition reactions of primary and secondary amine hydrogens with epoxy groups, (3) and parallely, autocatalyzed reactions by the OH groups produced during curing reactions. In this sense, the mechanistic kinetic model, assuming different reactivities of primary and secondary amine hydrogens, was defined by the following equations:

$$\left(\frac{dX}{dt}\right) = \left[K_1'(1-x-y) + K_1 y\right]\left[\frac{2(1-r)z_1 + rz_1^{r/2}}{2-r}\right] \tag{3}$$

$$\left(\frac{dz_1}{dt}\right) = -2z_1\left[K_1'(1-x-y) + K_1 y\right] \tag{4}$$

where

$$y = 0.5\left\{A - \left[A^2 - 4\left[C_0 + x(1-C_0) - x^2\right]\right]^{0.5}\right\} \tag{5}$$
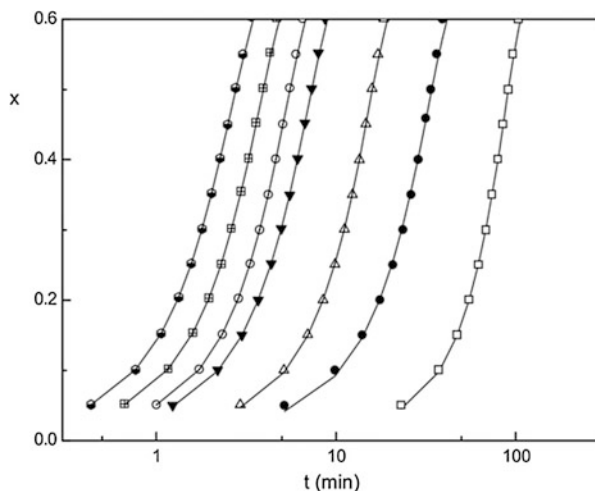
Fig. 10 Comparison between the mechanistic model (—) and experimental data at (□) 80 °C, (●) 100 °C, (Δ) 120 °C, (▼) 140 °C, (○) 150 °C (⊞), 160 °C, and (⊖) 170 °C for the blend modified with a 10 wt% block copolymer (Reprinted with permission Larrañaga et al. (2005))

Table 4 Values of the ratios of kinetic constants and the initial ratio of the epoxy group concentrations in blends and neat system (Reprinted with permission Larrañaga et al. (2005))

PEO–PPO–PEO (wt%)	K_{Blend}/K_{Neat}	K_{1Blend}/K_{1Neat}	K'_{1Blend}/K'_{1Neat}	e_{0Blend}/e_{0Neat}
10	0.75	0.72	1.86	0.89
20	0.68	0.55	1.98	0.79
30	0.60	0.43	2.23	0.68

$$A = 1 + C_0 + \frac{1}{K} \qquad (6)$$

$$x = \frac{e_0 - [e + (e - OH)]}{e_0} \qquad (7)$$

and

$$z_1 = \frac{a_1}{a_0} \qquad (8)$$

where e_0 and e denote the concentration of epoxy at time 0 and t, respectively, a_1 is the concentration of primary amino hydrogens, and r is the ratio of secondary to primary amino-hydrogen rate constants. The epoxy–hydroxyl complex formation is represented with the dimensionless equilibrium constants K. The autocatalyzed and uncatalyzed reactions are represented by the dimensionless kinetic constants K_1 and

K'_1, respectively; e-OH is the epoxy–hydroxyl complex concentration. C_0 is OH-equivalent/epoxy-equivalent and y is e-OH/e_0.

Figure 10 shows the fit of experimental curves with this mechanistic model for the epoxy system modified with 10 wt% PEO–PPO–PEO block copolymer at different curing temperatures. As can be seen, this model presented a satisfactory match with the experimental curves.

From the analyses of the kinetic parameters sumarized in Table 4, it was found a hindering in the formation of epoxy–hydroxyl complex and the autocatalytic process by blending compared with neat epoxy. On the contrary, it was observed that the constant for the uncatalyzed reaction of epoxy with amine increases with copolymer content. The diminution in K and K_1 values was ascribed to the fact that the iterations between the OH groups formed during curing with the block copolymer are more favored. In the case of K'_1, its increment was related to the fact that at early stages of reaction, less oxirane groups can interact with OH groups as the block copolymer content increases. In this sense, more oxirane groups are available for direct reaction with the amine. Therefore, from these results it was concluded that the influence of K and K_1 kinetics constants on curing rate is higher than the influence of K'_1 because even though the uncaltalyzed process was favored, the block copolymer delayed the curing reaction.

On the other hand, the effect of the interactions between the epoxy–amine system and the PEO–PPO–PEO block copolymers on the reaction rate depending on the molar ratio between blocks was also proved by isothermal DSC analyses (Larrañaga et al. 2006). Figure 11 shows conversion of epoxy groups vs. time curves obtained for the epoxy blends containing different amounts of EP-0.33:1, EP-0.8:1, and EP-3:1block copolymers cured at 140 °C. From these curves, it was noticed that the epoxy blends modified with copolymers containing different block molar ratio present a different delay even at the same content of modifier. This last fact proved that the delaying of cure kinetics is mainly due to physical interactions between the epoxy (OH groups initially existing and developed during the network formation) and PEO block (ether groups) than a dilution effect due to the content of modifier in the growing network system. As a result, the system that presented the higher delay on the curing reaction was the system modified with the block copolymer with higher PEO content. FTIR analyses corroborated these results because it was observed that when the PEO molar ratio in the block copolymer is higher, the associated hydroxyl group band appears at lower wave numbers. In addition, the intensity ratio between associated and free hydroxyl bands also increases. It was also pointed out that the hydroxyl–ether interactions modified the autocatalytic process causing a delay on the curing process. Figure 11b also shows the predicted curve from the kinetic model and the theoretical curve obtained taking into account the dilution effect for the epoxy system modified with 20 wt% of EP-0.8:1, an appropriate agreement was pointed out. In addition, it was also noticed that the curing reactions occur at a lower rate than when just the dilution effect was taken into account for the estimation. This last fact also corroborated the hypothesis that the interactions between the block copolymer and the epoxy significantly affect the curing behavior.

Fig. 11 Cure kinetics *curves* for epoxy systems cured at 140 °C containing 0 wt% (■), 10 wt% (○), 20 wt% (▲), and 30 wt% (□) of (**a**) EP-0.33:1, (**b**) EP-0.8:1, and (**c**) EP-3:1. In subpanel (**b**), *solid lines* show predicted curves from kinetic model for neat and 20 wt% EP-0.8:1, while *dashed lines* show a theoretical curve obtained by modeling dilution effect for 20 wt% EP-0.8:1 (Reprinted with permission Larrañaga et al. (2006a))
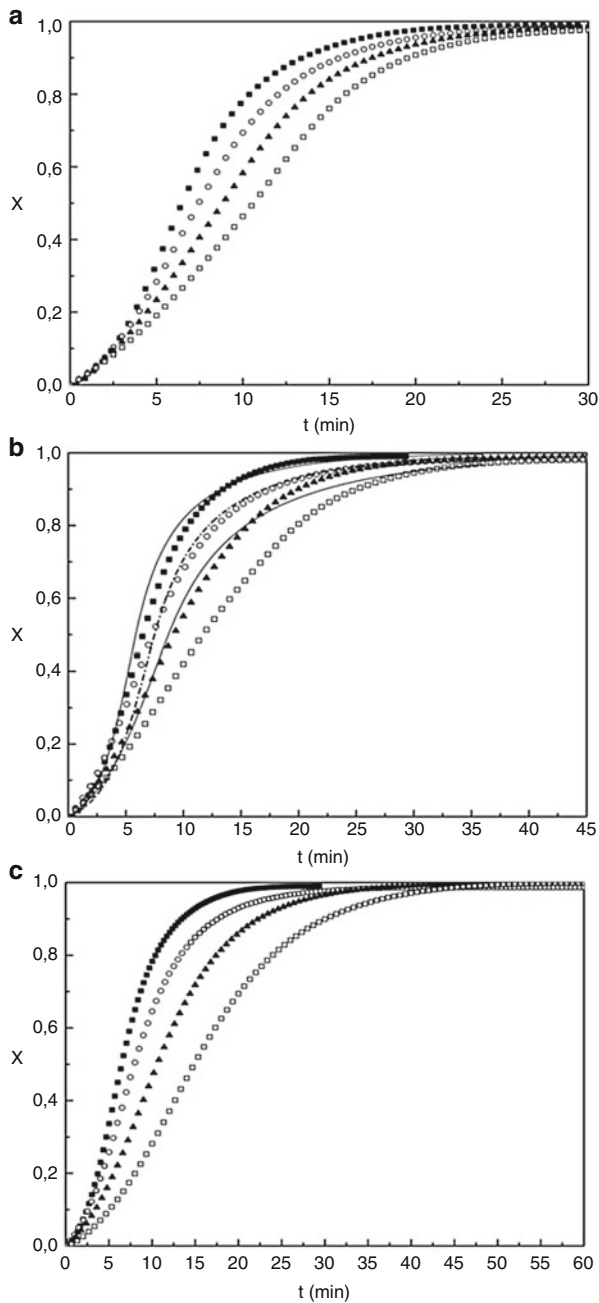
Table 5 Kinetic constants and concentrations of epoxy at initial time of block copolymer-modified epoxy systems with respect to those values for the neat system (Reprinted with permission Larrañaga et al. (2006a))

Modifier	Content (wt%)	K_{Blend}/K_{Neat}	K_{1Blend}/K_{1Neat}	K'_{1Blend}/K'_{1Neat}	e_{0Blend}/e_{0Neat}
EP-0.33:1	10	0.80	0.73	1.45	0.89
	20	0.77	0.61	1.69	0.78
	30	0.62	0.51	1.49	0.68
EP-0.8:1	10	0.75	0.72	1.86	0.89
	20	0.68	0.55	1.98	0.79
	30	0.60	0.43	2.23	0.68

Table 6 Activation energy and frequency factor values of block copolymer-modified epoxy systems (Reprinted with permission Larrañaga et al. (2006a))

Modifier	Content (wt%)	E_1 (kJ mol^{-1})	E'_1 (kJ mol^{-1})	ln (A_1 min^{-1})	ln (A'_1 min^{-1})
Neat matrix	0	49.0	61.8	13.9	13.2
	10	48.7	61.9	13.5	13.6
EP-0.33:1	20	49.6	62.0	13.6	13.7
	30	49.5	62.4	13.4	13.8
	10	49.7	62.1	13.8	13.9
EP-0.8:1	20	49.7	62.3	13.5	14.1
	30	49.7	62.5	13.3	14.2

The kinetics constants obtained by the use of this mechanistic approach, as average values in the 80–170 °C range, for epoxy blends with EP-0.8:1 and EP-0.33:1 compared with the corresponding epoxy system are summarized in Table 5. From these results, it was pointed out that in addition to the dilution effect, the interactions between components play an important role. This finding was ascribed to the fact that the ratio between the kinetic constants of the blend and the neat epoxy is different if they are compared with the ratio between the initial concentration of epoxy equivalents of the blend and the neat epoxy. From K and K_1 values, it was concluded that the formation of epoxy–hydroxyl complex and the autocatalytic processes are less restricted for the epoxy blends containing EP-0.33:1 than for the epoxy blend containing EP-0.8:1 when they are compared with the neat epoxy system. This behavior corroborated the fewer occurrences of physical interactions between components presented on the epoxy blend modified with the block copolymer containing lower PEO block content. Another finding was the increment of uncatalyzed kinetic parameter, K'_1, in the modified systems, and it is more evident in the case of the epoxy system modified with EP-0.8:1 due to its higher PEO content.

The activation energy and frequency factor values of the epoxy system modified with EP-0.8:1 and EP-0.33:1 compared with the corresponding epoxy system are summarized in Table 6. It was noticed that the activation energy values yield similar

values for all the systems. On the contrary, the frequency factors presented a slight variation, being higher for EP-0.8:1 than for EP-0.33:1 modified systems. In addition, the observed decrease of A_1 values was attributed to the delay of the autocatalytic process as a consequence of physical interactions between the components, while the increase of A'_1 values was related to the increase of epoxy groups that can react with the amine (Larrañaga et al. 2006).

The cure kinetic parameters of an epoxy system blended with ATPEI (amine terminated polyetherimide)–CTBN (carboxyl terminated poly(butadiene-co-acrylonitrile)) block copolymer, denoted as AB, were evaluated using isothermal DSC measurements and an autocatalytic model (Kim et al. 2005). Similar results to those discussed above about the effect on heat of reaction and final conversion of epoxy groups with the content of block copolymer were observed. Interestingly, this work proposed to take into account a rate equation with a diffusion control factor to explain the delay on curing process in the later stages of the reaction and to obtain a better match between the experimental values and the theoretical ones. The diffusion control factor f(X) is represented by the next equation:

$$f(X) = \frac{1}{1 + exp[C(X - X_c)]} \tag{9}$$

where C denotes the parameter of diffusion control and X_c is the critical value of cure conversion where reaction becomes controlled by diffusion. Therefore the final rate equation was rewritten as follow:

Table 7 Kinetic constants of the autocatalytic model for epoxy/DDS/AB blend systems (Reprinted with permission Kim et al. (2005))

Temp. (°C)	m	n	m + n	k_1 (min^{-1})	k_2 (min^{-1})
Epoxy/AB (0 wt%)					
160	1.0110	2.5410	3.5520	0.0070	0.0563
175	1.0213	2.3883	3.4096	0.0183	0.1241
190	1.0012	2.0346	3.0358	0.0274	0.1688
Epoxy/AB (10 wt%)					
160	1.0179	3.1792	4.1971	0.0069	0.0834
175	1.4494	2.8137	4.0610	0.0208	0.2027
190	1.4115	2.3171	3.7286	0.0366	0.2611
Epoxy/AB (20 wt%)					
160	1.0100	3.4210	4.4310	0.0042	0.0995
175	1.3213	3.0072	4.3285	0.0120	0.2288
190	1.2194	2.4750	3.6944	0.0245	0.2404
Epoxy/AB (30 wt%)					
160	1.0898	3.7662	4.8560	0.0050	0.1052
175	1.5328	3.1938	4.7266	0.0173	0.2432
190	1.4628	2.5251	3.9879	0.0287	0.3605

$$\frac{dX}{dt} = \frac{(k_1 + k_2 X^m)(1 - X)^n}{1 + exp[C(X - X_c)]} \tag{10}$$

Table 7 summarized the kinetic parameters calculated using this autocatalytic model including the diffusion phenomena. It was noticed that the values of n increased as the reaction rate decreased. This behavior was explained by the fact that for the epoxy blends, the reaction can be hindered by the phase separation process. On the other hand, the values of m oscillated around 1.0 even though when the block copolymer content was increased. This last fact revealed that neither the curing reaction nor the vitrification process has a significant effect on the autocatalytic behavior.

Figure 12 depicts the conversion versus reaction time at 160 °C, 175 °C, and 190 °C of the epoxy blends containing different amounts of AB. The calculated solid and dashed traces were obtained from Eqs. 1 and 10 with and without the diffusion control factor, respectively. From this study, it was noticed that the model including the diffusion control factor fitted quite well with the experimental data at the later stage of reaction, while the differences between the predicted values without the diffusion control factor and the experimental data were pronounced. This result indicated that, at the later stage of reaction, the diffusion control factor in the rate expression should be considered. It was also observed that the differences became more pronounced when the curing temperature used is low.

Finally, the curing kinetics studies for the epoxy system and its corresponding blends with 10, 20, and 30 wt% of eSBS (47 mol%) were conducted at different isothermal temperatures. The corresponding plot of conversion rate versus time is shown in Fig. 13. Similar results to those observed with the PEO–PPO–PEO block copolymer about the reaction rate delay with the increment of the block copolymer content in the blends were observed. This delay in this case was also attributed to a differential distribution of the epoxy–amine components in the epoxy-rich phase and in the block copolymer-rich phase, as a result of the phase separation process. The observed behavior on the extent of reaction with the time corroborated that the autocatalytic nature of the curing process was not affected by the inclusion of the block copolymer.

The kinetics parameters were calculated by the autocatalytic model (Eq. 1). The activation energy values and frequency factors are summarized in Table 8. It was found that the activation energy values increased with the amount of eSBS. This last fact was pointed out as another sign of cure reaction delay of epoxy system by the addition of eSBS. In addition, the same behavior of k_1 and k_2 with the content of block copolymer and temperature than that observed in Table 2 for the epoxy system modified with PEO–PPO–PEO was found.

Conclusions

Differential scanning calorimetry, both non-isothermal and isothermal mode, has demonstrated to be a very effective technique to study the curing process of epoxy/ block copolymer blends. The experimental cure kinetics curves of epoxy/block

Fig. 12 Degree of
conversion vs. time plot for
the cure process of epoxy/
DDS/AB systems;
experimental data (symbols)
and calculated data (lines) at
various isothermal conditions,
at 160 °C (**a**), 175 °C (**b**), and
190 °C (**c**) (Reprinted with
permission Kim et al. (2005))
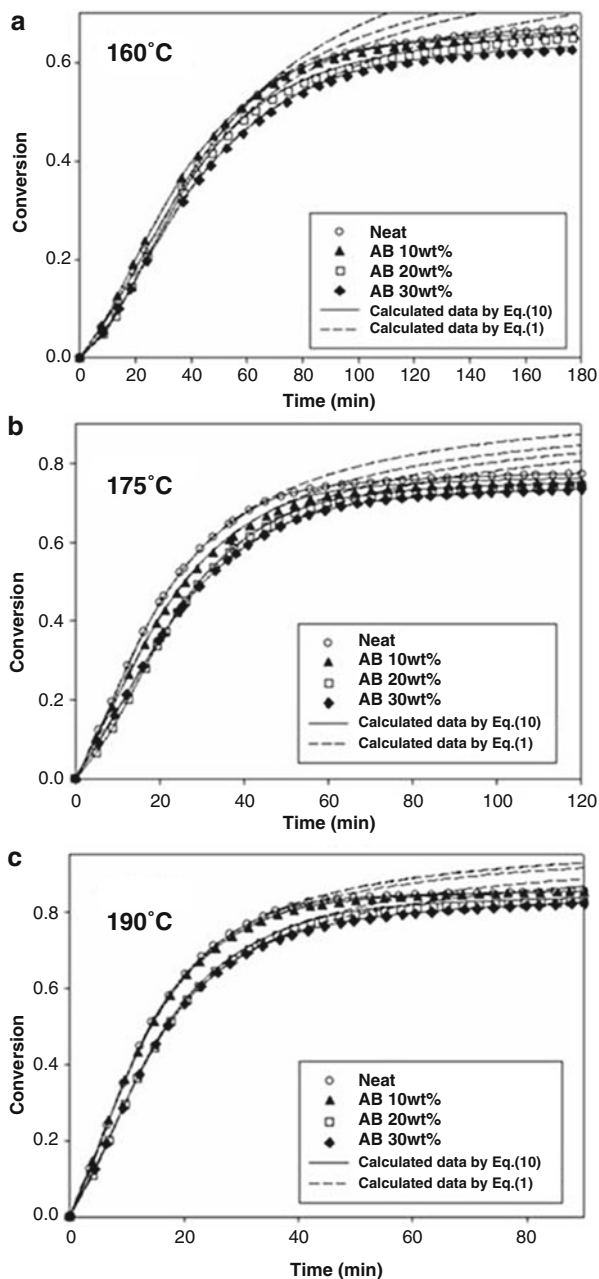
copolymer blends can be successfully fitted to both phenomenological autocatalytic
and mechanistic kinetic models. It has been observed that the cure kinetics during the
network formation of epoxy/block copolymer blends is affected by modifier con-
centration, volume fraction, chemical structure, and molecular weight of the blocks,

Fig. 13 Conversion rate vs. time curve for DGEBA/eSBS (47 mol%)/DDM (0, 10, 20, and 30 wt%) blends at 110 °C (Reprinted with permission George et al. (2012))
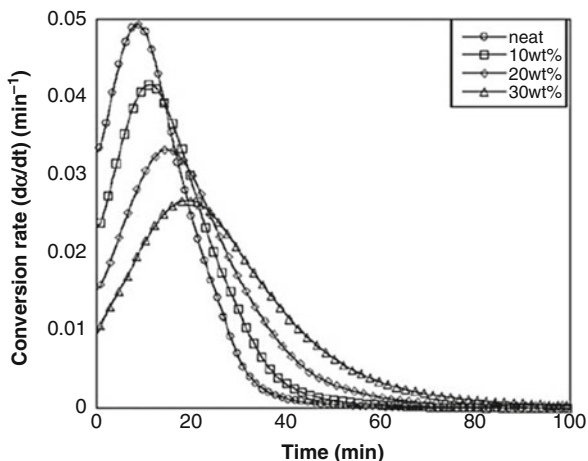

Table 8 The values of activation energy and frequency factor obtained for DGEBA/eSBS (47 mol%)/DDM system by Kamal approach (Reprinted with permission George et al. (2012))

wt% of eSBS in DGEBA/eSBS (47 mol%)/DDM	lnA_1	lnA_2	E_{a1} (kJmol^{-1})	E_{a2} (kJmol^{-1})
0	15.76	9.93	62.16	38.14
10	15.94	13.16	63.48	48.87
20	16.31	15.01	65.59	54.93
30	17.58	14.85	70.16	54.58

among others. Both DSC modes demonstrated that curing rate decreases as block copolymer content increases. The delay in reaction rate of epoxy/block copolymer blends can be attributed to the dilution effect due to a reduction in the density of reactive groups as the block copolymer content increases, interactions between blocks and the growing epoxy network which inhibits autocatalytic process, as well as a partial segregation of reactive monomers and oligomers to the block copolymer-rich phase. The delay in cure rate attributed to interactions between epoxy and block copolymer blocks was corroborated by FTIR analyses. However, it was observed that the presence of hydroxyl groups in block copolymers had a significant effect on the curing reaction. Isothermal curing was successfully fitted to a phenomenological autocatalytic model based on a semiempirical equation which takes into account catalytic and autocatalytic effects and also to mechanistic model accounting an epoxy–hydroxyl complex, uncatalyzed and parallel catalyzed reactions. Phenomenological autocatalytic model fitted quite well with the experimental conversion curves, and the observed small deviations at high conversion values were related to vitrification effects. The autocatalytic model including diffusion phenomena fitted quite well with the experimental data in the later stage of the reaction. Mechanistic model corroborated that in addition to dilution effect, the physical

interactions between components play an important role, and the observed delay is mainly due to these physical interactions than dilution effects. The kinetic parameters calculated from these mathematical models showed an increase in activation energies as block copolymer contents increase in agreement with the delay on curing rate observed.

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