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Molecular dynamics of an epoxy resin modified with an epoxidized poly(styrene–butadiene) linear block copolymer during cure and microphase separation processes

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ABSTRACT

Molecular dynamics of diglycidyl ether of bisphenol A (DGEBA) epoxy resin modified with an epoxidized poly(styrene-*b*-butadiene) (SepB) linear block copolymer has been monitored during cure and microphase separation process by dielectric relaxation spectroscopy (DRS) for wide frequency and temperature ranges. Different primary and secondary relaxation processes have been analyzed for neat components and ternary mixture. Relaxational behaviour has been modelled with Havriliak–Negami, Vogel–Fulcher–Tammann and Arrhenius equations and fitting parameters and their evolution have been obtained. The retention of the epoxidized poly(butadiene) (PepB) block in the epoxy-rich phase during all the polymerization process, previously detected by our group with atomic force and transmission electron microscopies, has been confirmed by dielectric relaxation spectroscopy. The evolution of molecular dynamics during the polymerization process of the epoxy resin in the ternary system indicates a change in the trend of the main relaxation at times that agree with phase separation detected by rheology.

1. Introduction

Block copolymers (BC) are the focus of a great deal of research activity because of their intrinsic ability to self-assemble into different nanoscale structures. This intriguing ability can be used to design new polymeric nanostructures with potentially interesting properties. In this way, amphiphilic block copolymers with one of the blocks miscible with the thermosetting matrix as well as reactive block copolymers containing specific groups in one of the blocks to promote chemical compatibilization, have been widely used for this purpose [1–10]. This pathway could lead to an improvement of both mechanical properties (notably fracture toughness) and stability of nanostructured materials [3–5,7]. Additionally, a second generation of block copolymers has been recently developed, proving that the nanostructuring of epoxy thermosets with block copolymers can be also prepared via reaction-induced microphase separation, starting from a homogeneous miscible blend [11,12]. As we recently reported [13–15], the epoxidation of commercial styrene–butadiene (SB) block copolymers, SepB, leads to the nanostructuring of the epoxy matrix through the microphase separation of PS block from the initially miscible multicomponent blend.

On the other hand, during the two past decades many investigations related with the evolution of primary and secondary relaxations in both neat and modified epoxy resins, before and during polymerization of the matrix, have been carried out by dielectric relaxation spectroscopy (DRS) [16–26].

A recent work of Beiner and Ngai [26], in which the authors make an exhaustive dielectric analysis of primary and secondary relaxations in polymerizable systems based on epoxy resins, can be distinguished. This work includes several published studies about the effect of reaction time, conversion or number of formed covalent bonds, unifying

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criteria by applying the 'coupling model' (CM) [27–30]. Besides the main α relaxation (related with segmental dynamics of the main polymer chains and considered as the dielectric manifestation of the glass transition temperature, T_g) in di- and triepoxide systems and also in their mixtures with amines and partially polymerized products, the presence of β and γ secondary relaxations has also been detected. For secondary relaxations, the temperature dependence of the relaxation time follows the Arrhenius law, while for the main α relaxation models like Kohlrausch–Williams–Watts (KWW) and Vogel–Fulcher–Tammann (VFT) are applied due to its non-linear dependence with reciprocal temperature. γ relaxation in pure epoxy systems is related with the dynamics of dipoles localized in edge epoxy groups (—CHOCH—), which is supported by two facts [26]: relaxation times remain unaffected when the epoxy resin is mixed with molecular liquids with lower mobility, and the relaxation disappears with the consumption of those groups. γ relaxation presents short relaxation times, $\tau_\gamma(\mathrm{s}) = 1/(2\pi f_{\max}/\mathrm{Hz})$, where $f_{\max}$ is the frequency corresponding to the maximum value of relaxation, in the range of nanoseconds at temperatures near T_g, while it does not seem to merge with the main relaxation at finite temperatures.

β relaxation, related to local dynamics of glycerol units ($—O—CH_2—CHOH—CH_2—$) by Mijovic et al. [31] (who identified this relaxation as $\beta*$), generally involves segmental dynamics of part of the polymeric chains (smaller than those corresponding to the main relaxation) [32]. The relaxation appears, at a constant temperature, at higher frequencies than the α relaxation and it can only be solved for temperatures near or lower than the T_g. Furthermore, the extrapolation of the Arrhenius type dependence of relaxation times in the glassy state at temperatures higher than the T_g shows an overlap with the relaxation times of the α process. Ngai and Beiner [26] observed also a decrease in the relaxation times of this transition in mixtures of di- and triepoxides with liquids with higher mobility, trend that was inverted after the polymerization reaction, increasing systematically. All these make β relaxation in epoxy systems, which leads to the appearance of the main relaxation, to be considered as Johari–Goldstein relaxation [33,34]. γ relaxation, present in the mixture before and during the polymerization reaction without significant changes in its position [18–20] and disappearing with reaction time due to consumption of epoxy groups, is considered as non-Johari–Goldstein secondary relaxation. It is worth to note that the γ relaxation is generally related with local motions of individual groups of atoms in the main chains, being in this way also attributed to amine groups [22,23,26,32].

Regarding the molecular dynamics related to microphase separation during the polymerization of epoxy resin in mixtures with block copolymers, the work of Mijovic et al. [31] must be distinguished. They monitored *in situ* and *in real time* both polymerization and microphase separation processes of poly(propylene oxide) (PPO) block in a reactive epoxy system modified with poly(ethylene oxide-*b*-propylene oxide) diblock, (PEO-*b*-PPO), and triblock, (PEO-*b*-PPO-*b*-PEO), copolymers. In the initial mixture, totally miscible, they observed the presence of β relaxations corresponding to the blocks of the copolymer, besides the presence of three relaxations corresponding to the epoxy resin. With the increase of reaction time, they found a displacement of the main α relaxation of the matrix towards lower frequencies emphasized due to the microphase separation process, appearing at frequencies lower than 0.1 Hz, as confirmed by the appearance of the α relaxation of the PPO block.

The aim of the present work is to analyze the molecular dynamics of a diglycidyl ether of bisphenol-A (DGEBA)/4,4′-methylene bis-(3-chloro-2,6-diethyl aniline) (MCDEA) epoxy system modified with 30 wt% of an epoxidized poly(styrene-*b*-butadiene) (SepB) linear block copolymer during cure and microphase separation processes, by dielectric relaxation spectroscopy. The evolution of relaxation processes with frequency and temperature is analyzed for both pure components and curing blends.

2. Experimental

The epoxy monomer DER 332 is a diglycidyl ether of bisphenol-A, kindly supplied by Dow Chemical. It had an epoxy equivalent of around 175 and an average number of hydroxyl groups per two epoxy groups $n = 0.03$. The hardener is an aromatic diamine, 4,4′-methylenebis(3-chloro 2,6-diethylaniline) (MCDEA), from Lonza. Their characteristics and structures are published elsewhere [14]. An amino-hydrogen-to-epoxy stoichiometric ratio equal to 1 was maintained for all mixtures. The diblock copolymer used in this work is a linear styrene-epoxidized butadiene copolymer, with an epoxidation degree of 46 mol %, SepB46. This copolymer has been epoxidized from a SB54 precursor (53.6 wt% PS, with a number average molecular weight of 46,000 g/mol and a polydispersity index of 1.2), synthesized by Repsol-YPF. The details of the epoxidation reaction and the physico-chemical characterization are described elsewhere [35].

2.1. Dielectric relaxation spectroscopy

DRS measurements have been carried out in a Novocontrol Alpha high resolution dielectric analyzer equipped with a Novocontrol Novocool cryogenic system for the temperature control, with simultaneous frequency (0.1 Hz to 4 MHz) and temperature (−100 to 40 °C) sweeps, registering both dielectric permittivity, ε', and dielectric loss, ε'', versus frequency at each temperature. Samples of raw components were prepared by solvent casting and evaporation of the solvent in vacuum. For reacting systems, samples of ternary copolymer/epoxy system containing 30 wt% SepB46 block copolymer have been prepared according to the following protocol: in a first step the copolymer and the epoxy resin are solved in toluene with the following evaporation of solvent by stirring at 60 °C. Then MCDEA is added at 90 °C and the mixture is stirred for 5 min and degassed in vacuum. The same protocol has been followed for neat epoxy system. Then, these blends have been cured between the electrodes of the dielectric analyzer, in an air oven at 140 °C. Samples have been extracted from the oven at several cure times and quenched into liquid nitrogen in order to stop polymerization reaction and obtain samples at different cure times.

2.2. *Differential scanning calorimetry (DSC)*

DSC measurements were performed using a Mettler Toledo DSC-822 calorimeter, calibrated with high purity indium. All experiments were conducted under a nitrogen flow of 20 mL min^{-1}, using 7–10 mg of samples in aluminium pans. Polymerization kinetics of neat DGEBA/MCDEA system has been analyzed by dynamic scans (−60 to 350 °C, 10 K min^{-1}) of samples placed in an air oven at 140 °C. Samples corresponding to different cure times were quenched into liquid nitrogen in order to stop the curing reaction. The analysis of the initial mixture ($t = 0$) gives the value of the reaction enthalpy of the initial mixture (ΔH_∞), while dynamic scans of the samples at each t times give the values of complementary or residual enthalpy (ΔH_t). Conversion of epoxy groups was obtained from the equation: $x = 1 - (\Delta H_t)/(\Delta H_\infty)$.

3. Results and discussion

3.1. *Molecular dynamics of raw components*

The dielectric relaxation spectrum corresponding to SepB46 copolymer has been analyzed by comparison with that of its precursor SB54, which is presented in Fig. 1. All dielectric spectra presented in the paper have been fitted (represented by solid lines in the figures) to Havriliak–Negami (HN) formalism, by using a HN term for each relaxation. The Havriliak–Negami formalism proposes an analytical expression for the complex dielectric permittivity as

$$\varepsilon^*(\omega) - \varepsilon_\infty = \frac{\varepsilon_0 - \varepsilon_\infty}{[1 + (i\omega\tau_0)^b]^c} \tag{1}$$

where $\varepsilon_0 - \varepsilon_\infty = \Delta\varepsilon$ is the dielectric strength, τ_0 is the central relaxation time, and b and c are parameters which describe the shape of the relaxation time distribution function (symmetric and asymmetric broadening). These parameters are obtained as fitting parameters. To describe the whole spectrum, the Havriliak–Negami equation must be combined with the following conductivity term for the temperatures at which it contributes:

$$\varepsilon_c'' = \left(\frac{\sigma}{\varepsilon_0\omega}\right) \tag{2}$$

where ε_0 denotes the vacuum permittivity and ε_c'' is the conductive contribution of the loss factor.

The α relaxation process, due to the segmental dynamics of the poly(butadiene) (PB) block, appears from −80 °C (at frequencies lower than 0.1 Hz), being centred at −60 °C at around 300 Hz. It is worth to note that the T_g of that block appears at around −80 °C, as determined by DSC measurements. On the other hand, the appearance of a secondary peak at higher frequencies (β_1 in Fig. 1) in this kind of copolymers has been attributed to their β relaxation [36]. It is known that β relaxation occurs at higher frequencies or lower temperatures than α process and both tend to overlap at the temperature known as 'merging temperature' [37,38], as it can be observed in the spectra corresponding to −50, −40 and −30 °C. In the case of SB copolymers, the molecular units that can contribute to the loss factor magnitude are styrene (phenyl group), vinyl and *cis*-1,4-PB units, because *trans*-1,4-PB ones do not present dipolar moment [36]. The dipolar moment of styrene units is lower than that of vinyl and *cis*-1,4 ones, which present similar dipolar moment [36,37]. In fact, several authors have shown that the dipolar response of PS is very week due to its non-polar character [39–42]. Runt et al. [42] incorporated a polar group into the phenyl ring for the detection of this β relaxation, whose activation energy, E_a^{PS}, is notably higher than that corresponding to PB [43], which, independently of the structure, has been determined as lower than 40 kJ/mol, implying that it is related to local motions [36,44]. Moreover, a third process at low temperatures, centred at around 1 kHz (named as β_2 in Fig. 1) can be also observed. That process appears at the same frequency than the β relaxation in poly(butadienes) with mostly 1,2-structure, at temperatures below their T_g [45]. Several studies have revealed that both α and β relaxations appear at higher temperatures/lower frequencies by increasing the amount of vinyl units in PB [45–49], which could justify the displacement of β_1 to higher frequencies in comparison with β_2. Cassalini et al. [50] studied α and β relaxations in PB containing mainly 1,4-units. In Fig. 4 of that reference, authors represent relaxation times of both relaxations by comparing with those corresponding to the relaxations observed for 1,2-PB by several authors [45,51]. Taking into account the ratio (both in frequency and temperature) among relaxation times of both processes, τ_β, β_1 and β_2 could be attributed to the β relaxation of the 1,4- and 1,2-units, respectively, already detected in PB with both microstructures [45].

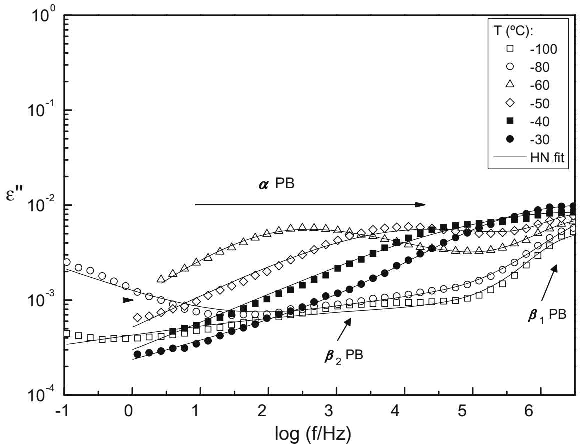


Fig. 1. Dielectric relaxation spectra for the SB54 copolymer. Solid lines indicate the fitting by Havriliak–Negami equation.

The molecular dynamics of SepB46 copolymer is analyzed in the following (Fig. 2). Spectra have been fitted to HN equation and fitting parameters are summarized in Table 1. It is worth to note that both PS and PB are basically non-conductive [52]. Epoxidation leads to an increase of PB

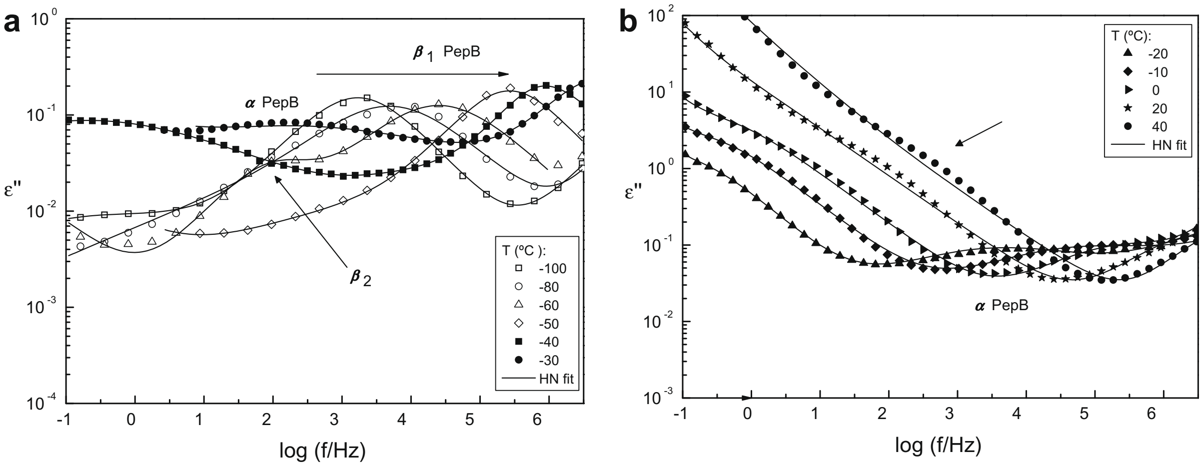


Fig. 2. Dielectric relaxation spectra of SepB46 copolymer at two temperature ranges. Different scales are presented for a better understanding. Solid lines indicate the fitting by Havriliak–Negami equation.

Table 1
Fitting parameters for the different relaxations for DGEBA:MCDEA system neat and modified with 30 wt% SepB46; at zero reaction time and mixed at 90 °C; as well as for neat SepB46 copolymer.

	β relaxation[a]			β relaxation[b]		γ relaxation[b]	
	τ_0 (s)	E_a (kJ/mol)	T_V (K)	τ_0 (s)	E_a (kJ/mol)	τ_0 (s)	E_a (kJ/mol)
DGEBA:MCDEA	2.99e-15	16.33	202.6	1.14e-15	48.12	–	–
30 wt% SepB46-modified	1.55e-14	16.14	189.9	1.00e-15	46.48	1.03e-08	6.34
SepB46	6.42e-11	4.73	176.5	(β_1) 1.27e-14 (β_2) 1.00e-20	(β_1)33.52 (β_2)68.96	–	–

[a] Relaxation time at infinite temperature, τ_0; activation energy, E_a; and Vogel temperature, T_V; according to Vogel–Fulcher–Tammann model.
[b] Relaxation time at infinite temperature, τ_0; activation energy, E_a; according to Arrhenius law.

polarity and, consequently, to an increase in the contrast among the dielectric response of different copolymers, as it can be seen by comparing Figs. 1 and 2a. In the low temperature range (Fig. 2a), three processes can be observed by increasing frequency: β_2 process, that is analyzed below; α process due to segmental motions (the T_g of the PepB block appears at −46 °C by DSC measurements) and the β_1 process, that moves to higher frequencies with temperature. This process would correspond probably to the segmental motion of the epoxy ring in the epoxidized poly(butadiene) block (PepB) of the main chain (*cis/trans*-PepB) because it shows an Arrhenius-like temperature dependence of relaxation times (estimated at $T < T_g$) with an activation energy, E_a, of about 33 kJ/mol, as it is shown in Table 1. Even more, the relaxation corresponding to oxirane group motions in neat DGEBA resin presents an E_a of the same order, ~28 kJ/mol [26,31,52]. The third process, named as β_2, presents an intensity similar to that of β_2 process in SB54 copolymer (compare scales in Figs. 1 and 2a), showing also Arrhenius-like temperature dependence ($E_a \sim 70$ kJ/mol, Table 1). Hsiue et al. [53], after performing temperature sweeps for epoxidized SB copolymers, observed the appearance of a peak below the T_g of PepB block, attributed to pendant epoxy groups resulting from the low epoxidation of 1,2-PB units, which present lower reactivity than 1,4-PB units [35].

In Fig. 2b, besides the α process, the appearance of a second process, indicated with an arrow, is also observed. That process could be attributed to the normal process of PepB block (it appears at lower frequencies than α relaxation) or to interfacial polarization mechanisms [37] associated to heterogeneous systems and observed for diblock copolymers [54]. The normal process has been observed, among others, for PEO-*b*-PPO type diblock copolymers associated with PPO block [31], for PI homopolymers and its copolymers (specially for *cis*-PI) [55,56], as well as for PEO-*b*-poly(butylene oxide) block copolymers (associated with the last block) [54]. For all of them a widening of the relaxation time distribution is observed, when compared with pure homopolymers. Regarding the interfacial polarization process, due to the bimodal distribution of the molar masses in the copolymer, which implies that there are mixtures of copolymers with different molar masses, it seems possible that at temperatures higher than the T_g of the PepB block (which implies mobility of PepB chains) this process takes place, appearing at lower frequencies. It is worth to note that changes in molar masses are due to epoxidation reaction, without affecting PS block. In order to elucidate if the process is related to the normal mode or to the interfacial polarization, the evolution of $\Delta\varepsilon$ (one of the HN fitting parameters) has to be taken into account. For the normal process, the magnitude of the relaxation or relaxation strength usually decreases when temperature increases [54]. As it can be seen in Fig. 3, $\Delta\varepsilon$ of the second process increases with temperature. Thus the evolution of the fitting parameter seems to indicate that the second process is related with interfacial polarization. The increase of its strength is probably due to the increase of conductivity with temperature, which leads to the increase of free charges which could be blocked in greater number at the interfaces.

The spectrum corresponding to neat DGEBA:MCDEA system at zero reaction time is presented in Fig. 4a for two temperature ranges (I and II).

Three relaxation processes can be observed by increasing temperature: β (in the temperature range between -80 and $-10\,^{\circ}C$), α (centred at around 1 kHz at $10\,^{\circ}C$), and γ (onset at around 1 MHz), associated to final epoxy groups and ($-NH_2$) type amine groups [32]. The secondary relaxations are Arrhenius-type processes, being the E_a values found in the literature for Goldstein–Johari β and γ processes in the neat DGEBA of around 39–47.6 and 25–28 kJ/mol, respectively [26,31,52]. Beiner and Ngai [26] found that the addition of ethylene diamine, with higher

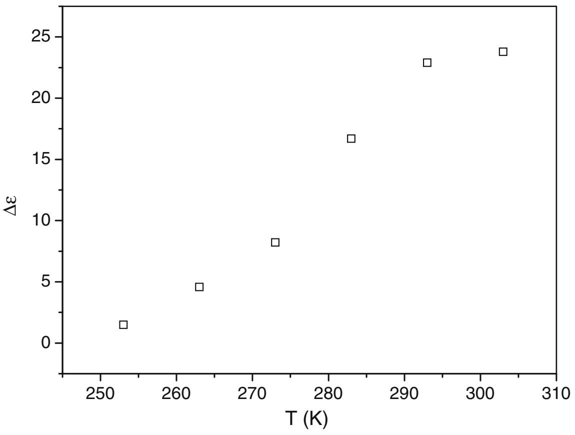
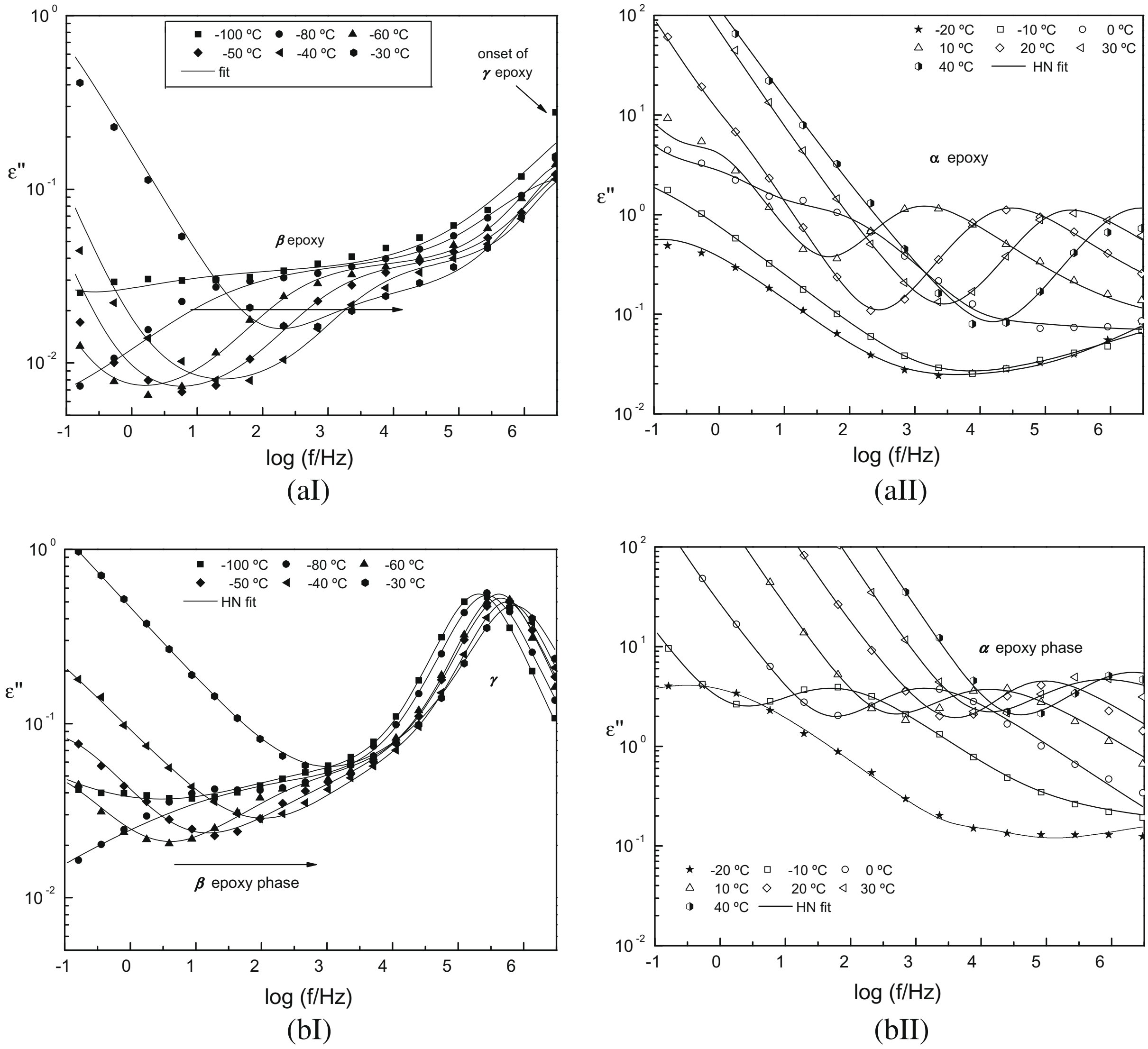


Fig. 3. Evolution of $\Delta\varepsilon$ (obtained from Havriliak–Negami fitting) with temperature for the relaxation process indicated by an arrow in Fig. 2b.



(aI) (aII)

(bI) (bII)

Fig. 4. Dielectric relaxation spectra of (a) neat DGEBA:MCDEA and (b) its blend containing 30 wt% SepB46; at reaction time 0 min; at the following temperature range: (I) -100 to $-30\,^{\circ}C$ and (II) -20 to $40\,^{\circ}C$. Solid lines indicate the fitting by Havriliak–Negami equation.

mobility than epoxy monomer, led to an increase in molecular mobility, making the β process to be faster in the initial mixture (the γ relaxation, due to its origin remained almost unaffected), which was justified by the diminishing of the configurational restriction (which implies an increase of the configurational entropy and specific volume) and by intramolecular interactions due to the higher mobility of the hardener. The mobility of MCDEA, however, is similar to that of the neat epoxy resin and lower than that corresponding to aliphatic amines. In fact, on one hand, both the height of the relaxation ($\Delta\varepsilon'' = 0.03$ at -80 °C) and the frequency of appearance are very similar to those published by Mijovic et al. for unmodified DGEBA (see Fig. 4 in Ref. [31]): -80 °C/$\sim$20 Hz, -60 °C/$\sim$200 Hz, etc., seeming that the relaxation is not affected. On the other hand, the activation energy of the process, obtained by fitting temperature dependence of relaxation times to Arrhenius equation is $E_a^{\beta} = 48$ kJ/mol, as shown in Table 1, in the order of that found for the neat resin.

Dynamics of the ternary systems should differ from those corresponding to pure components. The ternary system (Fig. 4b) presents the same relaxations previously described: α, β and γ relaxations. The α process appears from lower temperatures than in the neat system, which implies that it is associated with combined cooperative segmental motions of DGEBA and PepB block in the blend, thus indicating, as was expected [15], their miscibility. In the low temperature range (part I of Fig. 4b) it can be observed that, while β process remains almost unaltered, γ relaxation appears at notably lower frequencies, with longer relaxation times. β Arrhenius-like process, presents an activation energy of $E_a^{\beta} = 46$ kJ/mol for SepB46-modified system, similar to that found for neat epoxy resin (Table 1). In fact, the comparison of the spectra obtained for raw components and ternary mixture at three temperatures (Fig. 5) clearly shows that β relaxation appears almost unaltered respect to that of the epoxy system (centred at around 10 and 250 Hz, at -80 and -50 °C, respectively), while no contribution of the β relaxation of the copolymer is observed (which can be masked). So it is mostly attributed to DGEBA resin.

Regarding γ process, it is worth to note that its origin is due to the localized motion of atom groups, being attributed in epoxy/amine mixtures to epoxide and -NH_2 groups [32]. As observed for initially miscible PEO-*b*-PPO/epoxy mix-

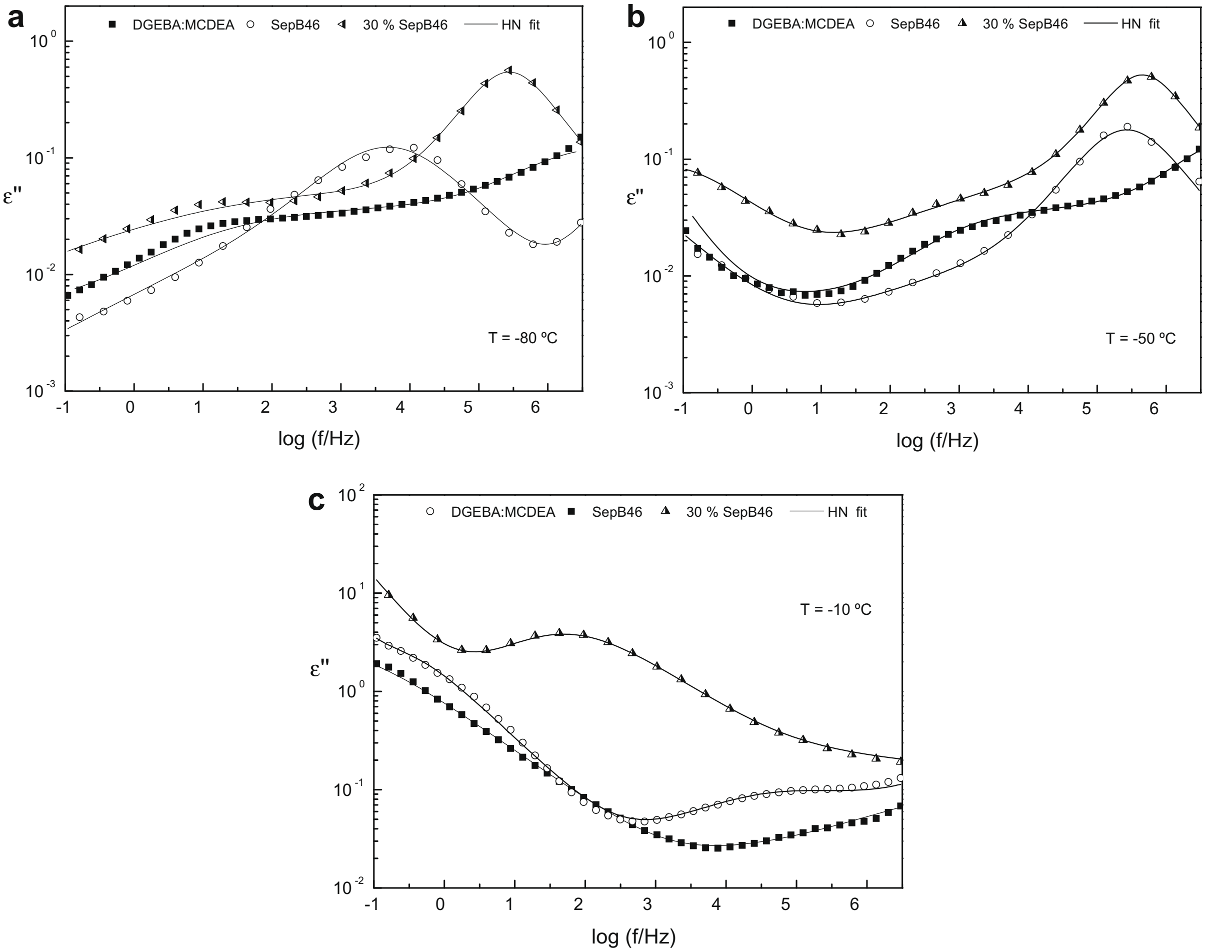


Fig. 5. Dielectric relaxation spectra for SepB46 copolymer; neat DGEBA:MCDEA system and 30 wt% SepB46-modified system; at zero reaction time; measured at different temperatures. Solid lines indicate the fitting by Havriliak–Negami equation.

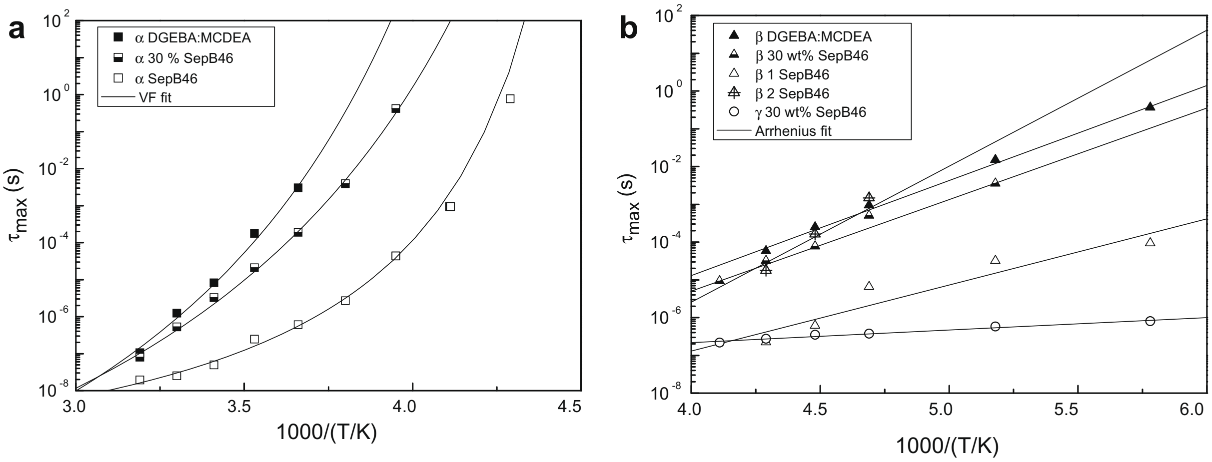


Fig. 6. Representation of the relaxation times obtained from the frequency of the maximum ($\tau_{max} = 1/(2\pi f_{max})$) of the dielectric loss after HN fit for different relaxations of the DGEBA:MCDEA system neat and modified with 30 wt% SepB46; for zero reaction time and mixed at 90 °C; as well as for the SepB46 copolymer: (a) α relaxation times fitted to Vogel–Fulcher–Tammann model; and (b) β and γ relaxation times fitted to Arrhenius law.

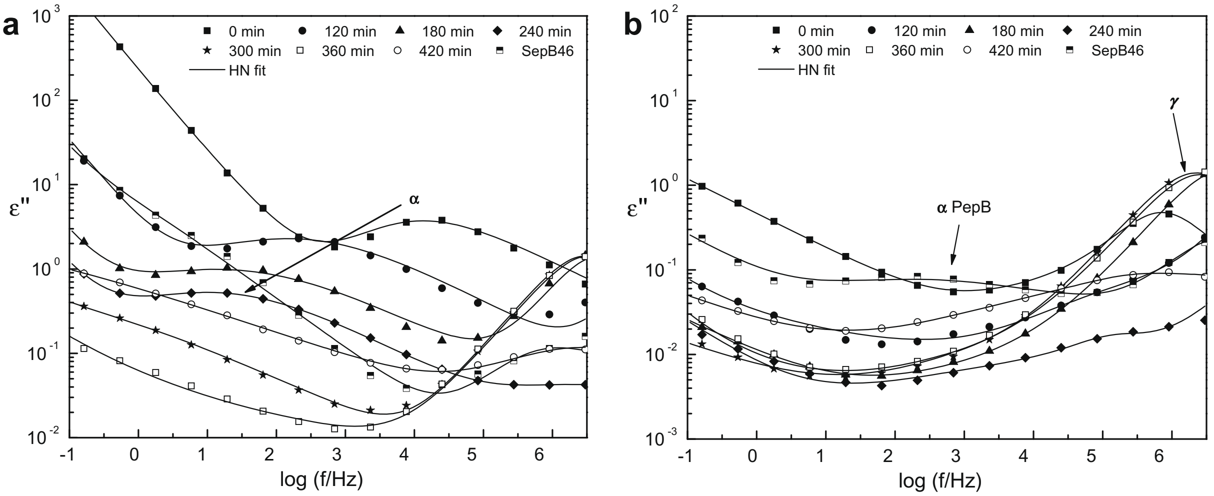


Fig. 7. Dielectric relaxation spectrum for 30 wt% SepB46-modified system cured for several times at 140 °C; measured at: (a) 10 and (b) −30 °C. The spectrum corresponding to the SepB46 copolymer is included for comparison. Solid lines indicate the fitting by Havriliak–Negami equation.

tures, the γ relaxation of the epoxy system is not affected and moreover, the β relaxation corresponding to both PEO and PPO blocks is detected [31]. For SepB46-modified system, the origin of this γ process is not clear. The β relaxation of the copolymer is not observed (compare Fig. 5a and b, the β relaxation of the copolymer moves in the frequency range, while γ relaxation in the ternary system is not moving).

There are, thereby, two possibilities: (i) the γ process to be consequence of the displacement of γ process of the neat epoxy resin towards lower frequencies in combination with the corresponding β process of the copolymer, or (ii) the γ process of the resin appears at frequencies higher than 1 MHz and the observed process is due to some kind of interaction between epoxy groups of the copolymer and the hardener. The addition of the copolymer with a notably higher viscosity than the epoxy monomer and the fact that in the analyzed temperature range (−100 to −40 °C) the PS block is below its T_g, decreases considerably the mobility of the ternary mixture comparing with the neat epoxy system. Moreover, as it can be observed in Fig. 5c, this relaxation disappears apparently from −20 °C, temperature at which β relaxation of epoxy matrix begins (Fig. 4bI at high frequencies), though the height of α process at high temperatures and frequencies increases. Thus this relaxation could probably be consequence of motions of atoms groups (due to the value of relaxation times presented below in Fig. 7) belonging to the copolymer, that weakly interact with the system at $T < T_g$, interactions that apparently disappear after the glass transition due to the chain mobility.

In Fig. 6, relaxation time reciprocals are shown for the different relaxations corresponding to the neat and 30 wt% SepB46-modified DGEBA/MCDEA systems as well as for the raw copolymer, as obtained from Havriliak–

Negami fitting procedure. Solid lines indicate fitting to Arrhenius or Vogel–Fulcher–Tammann functions, with the characteristic fitting parameters summarized in Table 1. Due to the trend of relaxation times of both β and γ Arrhenius type relaxations, as well as that of the non-Arrhenius α relaxation, and comparing with trends published in the literature, the assignation is corroborated. The data dispersion in the case of the β process of the copolymer (identified as β_1 in Fig. 2) is due to the presence of another β relaxation (identified as β_2 in Fig. 2) in the low temperature range. Concerning the non-Arrhenius α relaxation, T_g values estimated from DRS data for neat and modified epoxy systems (by the non-rigorous extrapolation at $\tau_{max} = 100$ s in Fig. 6) are around −10 and −30 °C, respectively, in good agreement with T_g obtained by DSC measurements and corroborating the miscibility between PepB block and epoxy matrix in all the temperature range analyzed. Moreover, the Vogel temperatures estimated are in good agreement with the usual relationship T_g (K) = T_v (K) + 50 K [57]. It is also observed that in the same temperature range, the displacement of α relaxation in epoxy system is larger than that of the same process in the modified one, which agrees with the lower mobility of the ternary system, due to the heterogeneity of the multicomponent system and its higher viscosity. Finally, the comparison of the evolutions of β processes in the reactive mixtures underlines the higher activation energy for the SepB46-modified system, suggesting some interactions among the copolymer (probably by epoxy groups of the PepB block) and epoxy resin, which modifies the relaxational behaviour. Similar trends have been observed by Mijovic et al. [31] for PEO-*b*-PPO/epoxy systems.

3.2. Molecular dynamics during cure and microphase separation processes

Dielectric relaxation spectra of 30 wt% SepB46-modified system cured for different times at 140 °C are shown in Fig. 7a and b for measurements carried out at 10 and −30 °C, respectively, taken as representatives of the cure process. It is worth to note that in spite of preparing the initial sample at 90 °C, both rheological and DSC measurements have revealed total miscibility for the multicomponent system after 10 min of cure at 140 °C. Moreover, after 120 min of cure at 140 °C, while DGEBA conversion for the neat system is around 0.2, the corresponding conversion for the modified one is lower (~0.1 as determined by DSC), due to the delay produced by the addition of 30 wt% SepB46. Thus, data obtained in this section can be considered as the result of isothermal curing at 140 °C, being the system initially fully miscible. For assuring those conditions, first data is taken after 120 min of cure.

At 10 °C, the α process (centred at about 20 kHz for zero cure time) moves to lower frequencies with cure time as a consequence of the global diminishing of the segmental mobility during the formation of the thermosetting network, which involves a decrease of the relaxation intensity, together with its broadening (Fig. 7a). Although not shown here, the corresponding spectra at 20 °C shows that for cure times longer than 240 min, this relaxation, associated to the polymerization reaction, moves towards frequencies lower than 0.1 Hz. That time, 240 min, coincides with the onset of phase separation detected by rheology, which is completed after 300 min, while the gelation process taking place at about 360 min [15]. Mijovic et al. [31] observed the same phenomenon for an epoxy matrix modified with PEO-*b*-PPO and PEO-*b*-PPO-*b*-PEO block copolymers. In fact, while the α relaxation of the PepB block in the pure copolymer is detected at −30 and −20 °C in the analyzed frequency range (Fig. 4), measurements carried out at −30 °C for the SepB46-modified system (Fig. 7b) indicate that the PepB block remains in the epoxy matrix (due to its miscibility with the thermosetting formulation [15]), as indicated by the absence of the β relaxation of PepB block independently of cure time. The detection of the relaxations corresponding to PS block is complicated because, as commented above, the dipolar response of PS is very weak due to its non-polar character [17,58,59], and its β relaxation is very difficult to detect, though it would appear in the analyzed frequency/temperature range. Consequently, in the following the analysis is focused on

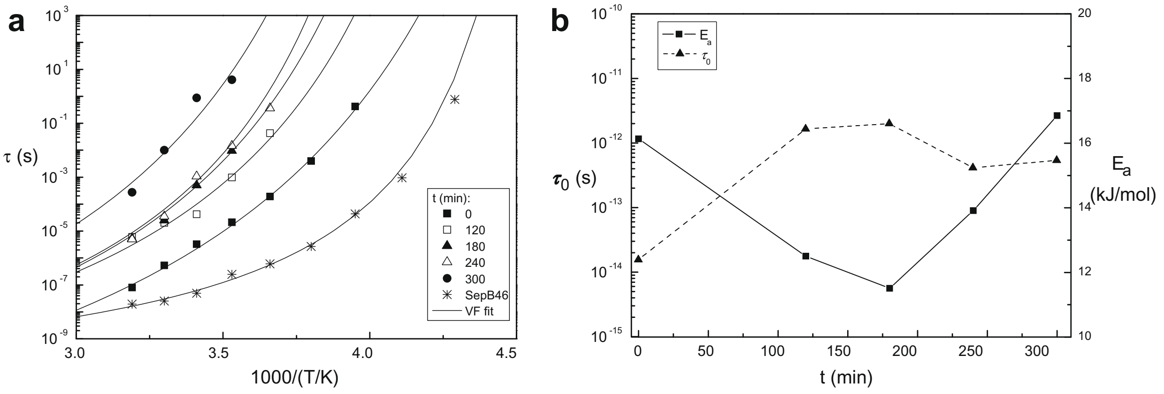


Fig. 8. (a) Evolution of relaxation times of α relaxation for 30 wt% SepB46-modified system with curing time at 140 °C obtained from $\tau_{max} = 1/(2\pi f_{max})$ after NH fit. The solid lines show the description by the VFT model; where values of the Vogel–Fulcher temperature; T_v; are shown with the legend. The evolution of α relaxation of PepB block in neat SepB46 copolymer has been included for comparison. (b) Evolution of the relaxation time at infinite temperature, τ_0; and activation energy; E_a; fitting parameters with curing time at 140 °C for 30 wt% SepB46-modified system; according to Vogel–Fulcher–Tammann model.

the variation of the main relaxation of the epoxy-rich phase.

Fig. 8a shows the relaxation time reciprocals, obtained from the Havriliak–Negami fitting procedure, for the α relaxation of the epoxy-rich phase for 30 wt% SepB46-modified epoxy system at several cure times at 140 °C. Solid lines indicate fitting to Vogel–Fulcher–Tamman equation, with Vogel temperatures indicated in the legend. The corresponding evolution of τ_0 and E_a fitting parameters is shown in Fig. 8b. It can be clearly seen the change of the trend of the main relaxation of the matrix from 240 to 300 min of reaction, time in good agreement with that determined by rheology [15]. It should be noted that rheokinetic analysis of this system has revealed that PS block begins to microseparate around 250 min, while gelation process of the epoxy phase takes place at around 360 min of curing at 140 °C [15].

The onset of the phase separation process implies an initial decrease of the T_g of the epoxy-rich phase, as indicated by the tendency of T_v, due to the separation of the component with the higher T_g. This decrease comes accompanied with the increase of the mobility of the epoxy phase due to two reasons: the component that microphase separates is solid at the analyzed temperatures ($T < T_g^{PS}$), and on the other hand, the relative epoxy mass fraction in the epoxy-rich phase increases as a consequence of microphase separation process. Once microphase separation takes place, which occurs not very far away from gelation process, a more and more accused increase of the T_g is expected. Similarly, a change in the tendency of both τ_0 and E_a with curing time can be observed from 240 min. As it has been reported for neat DGEBA/MDA (methylene dianiline) system [60], a decrease of E_a occurs up to the gelation process (from epoxy conversion of around 0.35) – associated to the fact that secondary amine-epoxy reactions become important and a cross-linked network begins to form – but, once gelation takes place, it begins to increase again up to a conversion of 0.6, due to the steric hindrance and the intermolecular rigidity of the network. In our case, however, gelation process occurs after 360 min of curing, which would imply that the observed changes may be related to microphase separation process. In order to clarify this point, kinetics of polymerization of both systems has been briefly analyzed. Fig. 9 shows the evolution of conversion for DGEBA/MCDEA system at 140 °C (data obtained as described in Section 2). As it is well known, in the stoichiometric balanced system the gel point is reached at a degree of conversion of 0.59, which corresponds to a reaction time of 240–250 min at 140 °C [61]. Experimental data have been fitted to the model employed by Eloundou et al. [61a] for the DGEBA/MCDEA system, at 140 and 160 °C, obtaining similar values for the different constants. The theoretical conversion curve for 30 wt% SepB46-modified system up to phase separation process has been predicted by taking into account the dilution effect. As it can be seen, phase separation process takes place in the epoxy conversion range of 0.35–0.5 (240–300 min), which implies that the decrease of E_a values observed in Fig. 7b could be influenced by the epoxy polymerization [60].

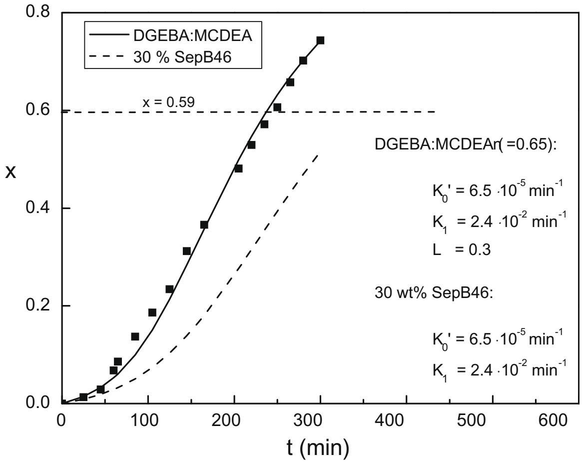


Fig. 9. Conversion evolution versus cure time at 140 °C for neat DGEBA/MCDEA system. Solid lines correspond to model conversion curves at 140 °C for neat DGEBA:MCDEA system (fitting of the data to the model of Elondou et al. [45]) and its blend containing 30 wt% SepB46 (from the data for neat epoxy system taking into account the dilution effect). For SepB46-modified system; the modified constants K_0' and K_1; have been calculated through the $(K_0')_{mod} = K_0'[(e_0)_{mod}/(e_0)_{neat}]^2$ and $(K_1)_{mod} = K_1[(e_0)_{mod}/(e_0)_{neat}]$ relations [62]; by using the densities of the unreacted epoxy system at 140 °C (1.1 g cm^{-3}) [63] and the copolymer. Fitting parameters for both systems are shown with the legend.

Nevertheless, those values begin to increase from 240 min, at the onset of phase separation, while gelation process takes place around 360 min, which allows us to conclude that it is mainly related with the microphase separation process. The exact mechanism remains unclear at present but the authors believe that it should be related with the fact that reaction-induced microphase separation of PS block leads to the self-assembly of PS cylinders, of around 40 nm of diameter, in an epoxy-rich phase, which forms the matrix [15]. Consequently, even if the separation of the rigid component causes an initial increase in the mobility of epoxy resin, this separation occurs at nanoscale, which means that PS may hinder the mobility of the epoxy-rich phase thus increasing the activation energy of the α process before gelation. In addition, FTIR spectra of cured blends have revealed the formation of intramolecular hydrogen bonds presumably associated to unreacted epoxy groups of the copolymers and the epoxy network [15], thus it is also possible that the interaction between PepB block and the epoxy system hinders the reorientational motions of terminal epoxy groups (which are the heart of the α process), contributing to this increase.

4. Conclusions

Molecular dynamics analysis of DGEBA:MCDEA epoxy system, an epoxidized SepB46 copolymer and their mixture during cure and microphase separation processes has been carried out.

Dielectric analysis of the synthesized raw SB54 diblock copolymer reveals the presence of the α relaxation of PB block between −80 and −60 °C, and β relaxations corresponding to 1,4- and 1,2-PB units. For the case of epoxidized SepB46 copolymer, besides β relaxations associated to the chains of the PepB block, with an activation energy of about 33 kJ/mol, and to epoxidized vinyl units, a third process has been detected at higher temperatures/lower frequencies than α relaxation of PepB block. This process can be related to the normal mode of PepB or to an interfacial polarization process, due to the bimodal molar mass distribution of the copolymer. The increase of the fitting parameter $\Delta\varepsilon$ (relaxation strength) with temperature seems to relate the process to the interfacial polarization. For the normal mode, $\Delta\varepsilon$ usually decreases with temperature. Finally, the α relaxation of the epoxidized copolymer has been estimated to appear at about −50 °C, slightly higher than that detected by DSC.

The analysis of the reactive mixtures at zero time reveals the presence of both α and β relaxations of the epoxy resin (or those of epoxy-rich phase in the mixture). For the case of the modified system (30 wt% SepB46), a decrease in the α relaxation of the epoxy-rich phase corroborates the initial miscibility of the PepB block. Additionally, an Arrhenius-type process appears at high frequencies and temperatures lower than those corresponding to the α relaxation of the system, believed to be consequence of the weak interaction between the copolymer and the thermosetting formulation, due to the fact that activation energy is much lower than those corresponding to the secondary relaxations of pure epoxy and pure copolymer.

For the same temperature range the α relaxation of the neat epoxy system has a larger displacement than that of the corresponding ternary system, which agrees with the lower mobility of the modified system due to the heterogeneity of the multicomponent system and the higher viscosity, besides a decrease in the temperature of appearance due to the miscibility with PepB block. The corresponding evolution of β process indicates higher activation energy for the ternary system, as a consequence of the interaction between the epoxy groups of the PepB and the epoxy resin.

The retention of PepB block in the epoxy-rich phase during all the polymerization process, previously detected by rheokinetic analysis [15], has been confirmed by dielectric relaxation spectroscopy. The evolution of molecular dynamics during the polymerization process of the epoxy resin in the ternary system indicates a change in the trend of the main relaxation at times that agree with phase separation detected by rheology. A change in the trend of fitting parameters has been detected at times that agree with the microphase separation process of the PS block. It should be related with the fact that reaction-induced microphase separation of PS block leads to the self-assembly of PS cylinders, of around 40 nm of diameter, in a epoxy-rich phase, which forms the matrix. Consequently, even if the separation of the rigid component causes an initial increase in the mobility of epoxy resin, this separation occurs at nanoscale, which means that PS may hinder the mobility of the epoxy-rich phase, increasing the activation energy of the α process before gelation.

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