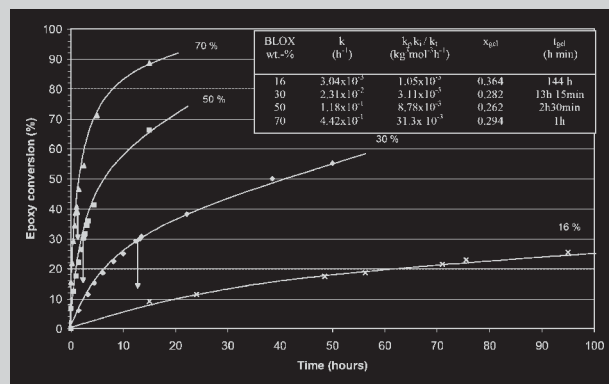


**Summary:** A thermoplastic poly(hydroxyl-amino ether) polymer (BLOX) was blended with a diglycidyl ether of bisphenol A monomer (DGEBA). This system may be used as a crosslinkable thermoplastic. It means that it may be processed in an extruder like a classic thermoplastic, and cured by etherification reactions initiated by tertiary amine groups of the BLOX in a second step, to produce a material with good mechanical properties. In order to understand and quantify the etherification reactions occurring at high temperature (135 °C), between epoxy groups of the diepoxy and hydroxyl groups of the thermoplastic, a model system was studied based on DGEBA in excess and ethanolamine. In the model system the rate of the etherification reaction was well described by a second-order kinetic equation. The specific rate constants and the epoxy conversion at the gel were related to the polarity of the reactive medium. The polyetherification occurring in the DGEBA-BLOX system could also be fitted with a second-order kinetics. A significant increase in the

reaction rate was observed when using high BLOX concentrations.



## Post-Crosslinkable Blends: Reactions Between a Linear Poly(hydroxyl-amino ether) and a Diepoxy

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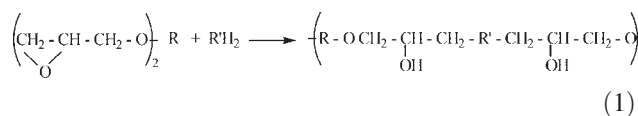
**Keywords:** blends; epoxy etherification; poly(hydroxyl-amino ether); post-crosslinkable thermoplastic; thermosets

### Introduction

The synthesis of thermosetting polymers, or thermosets (TS), through the reaction of epoxide compounds like diglycidyl ether of bisphenol A (DGEBA) and amines, is well known in literature.<sup>[1]</sup> These polymers are found in a broad range of applications that include adhesives, coatings and composites. Epoxies have generally excellent adhesion to different substrates, outstanding corrosion resistance, and also excellent barrier properties to atmospheric gases. These barrier properties are a partial consequence of the strong contribution of their pendant hydroxyl groups to intermolecular cohesion via interchain hydrogen bonding.<sup>[2]</sup> For all these reasons TS epoxies are used as coatings for packaging applications.

Despite the spectacular success of TS epoxies, very few examples of high molar mass thermoplastic (TP) epoxy

polymers have been reported. Linear or branched poly(hydroxyl ethers), usually named phenoxy, are prepared by direct reaction of bisphenol A with epichlorohydrin. Recently the stoichiometric-balanced polyaddition of diepoxides with dinucleophilic monomers has been generalized (Equation (1)),<sup>[3]</sup> and a broad range of TP polymers with good adhesive and barrier properties have been prepared.



Monoamines like ethanol amine (EA) react cleanly with pure DGEBA at 150–180 °C in the melt, in a conventional extruder and without any catalyst, to yield a soluble poly(hydroxyl amino ether) TP.<sup>[4,5]</sup> The mechanism of the reactions between –NH<sub>2</sub> and oxirane are well established.<sup>[6–11]</sup>

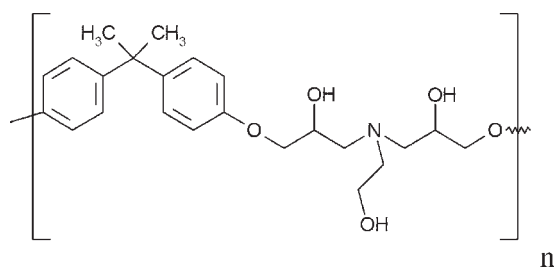
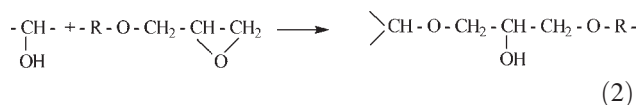


Figure 1. Chemical structure of poly(hydroxyl-amino ether), BLOX 00™ (trademark of the Dow Chemical Company).

Beside these reactions between primary and secondary amino groups and oxirane, a side reaction between the formed hydroxyl groups and oxirane can occur (Equation (2)).



This reaction is initiated by the presence of a Lewis acid or a base, like a tertiary amine.<sup>[12–18]</sup> For this reason the key to the successful synthesis of melt stable linear polymers is to work with a slight excess of monoamine to control the desired molar mass but also the nature of chain ends and to be sure to have no residual epoxy group.<sup>[4–5]</sup> The final polymer possesses one primary hydroxyl group (from EA), two secondary hydroxyls and one tertiary amine (from the reaction indicated in Equation (1)), per repeating unit (Figure 1).

Chain ends are secondary amino groups from partially reacted EA excess:  $\text{-NH-(CH}_2\text{)}_2\text{OH}$ .

In a previous paper<sup>[19]</sup> it has been demonstrated that these poly(hydroxyl-amino ethers) or BLOX polymers can be blended with liquid DGEBA by the use of a twin-screw extruder. Soft processing conditions,  $\approx 180^\circ\text{C}$  during less than 3 min, enabled to prepare new TP/TS epoxy blends. The TP is miscible in DGEBA but due to the presence of epoxy groups with large amounts of hydroxyl and tertiary amines, reactions like Equation (2) are expected to occur. It means that after a first process as a TP, the blend can be post-crosslinked.

The aim of this work is to study the possibilities of post-reactions and to define the post-curing conditions of these processable blends. For this purpose, a low molar mass model system based on an excess of liquid DGEBA pre-reacted with EA will be studied first. A model for epoxy homopolymerization/etherification will be developed and applied to the behavior of DGEBA-BLOX blends. Conditions to obtain a crosslinked polymer after blend extrusion will be defined.

## Experimental Part

### Products

The epoxy monomer was a standard DGEBA, DER330 from DOW, used without further purification. This prepolymer with

Table 1. Initial compositions of DGEBA-EA solutions.  $r$  is the ratio between initial amine and epoxy groups ( $[\text{NH}]_0/[\text{E}]_0$ ),  $[\text{E}]_0$  is the concentration of epoxy groups,  $[\text{OH}]_0$  is the concentration of hydroxyl groups.

DGEBA/EA mass ratio	$r$	$[\text{E}]_0$	$[\text{OH}]_0$
		$\text{mol} \cdot \text{kg}^{-1}$	$\text{mol} \cdot \text{kg}^{-1}$
100/4	0.247	5.029	1.001
100/5	0.328	4.968	1.187
100/7	0.481	4.855	1.529
100/10	0.658	4.731	1.911

a degree of polyaddition of  $\bar{n} = 0.15$  contains few hydroxyl groups. Ethanolamine, EA, was a liquid amine purchased from Aldrich (99% purity).

The poly(hydroxyl-amino ether) thermoplastic BLOX™ polymer was supplied by DOW. Its main characteristics were a number average molar mass equal to  $12.8 \text{ kg} \cdot \text{mol}^{-1}$ , a polydispersity index of 2.8 and a glass transition temperature close to  $72^\circ\text{C}$ . It is important to note that, due to the operating conditions during BLOX synthesis, chains ends of BLOX were secondary amino groups  $\text{-NH-(CH}_2\text{)}_2\text{OH}$ . The thermoplastic contained also 5/1 000 wt.-% of aminoethyl ethanolamine (AEEA)  $\text{H}_2\text{N-(CH}_2\text{)}_2\text{-NH-(CH}_2\text{)}_2\text{OH}$  for better thermal stability of the polymer.

### Sample Preparation and Techniques

Blends of DGEBA with ethanolamine were prepared at room temperature by mixing manually during 30 sec appropriate amounts in glass tubes. The proportions of the two reactants are indicated in Table 1. The thermoplastic BLOX/DGEBA blends containing 30, 50 and 70 wt.-% of BLOX were prepared with a co-rotating twin-screw extruder as described in a previous publication.<sup>[19]</sup> The blend with 16 wt.-% of BLOX was obtained by dissolution of the 30 wt.-% sample in the appropriate amount of DGEBA.

Glass tubes containing the samples were introduced in an oven. After heating at  $135^\circ\text{C}$  during selected times, the samples were taken off and cooled down to stop further reactions. Tetrahydrofuran (THF) was then introduced in order to obtain solutions at  $5 \text{ g} \cdot \text{l}^{-1}$ . The solutions were filtered ( $0.22 \mu\text{m}$  pores) before chromatographic analysis.

Size exclusion chromatography (SEC) was employed to measure the extent of epoxy-amine and epoxy-epoxy reactions. The SEC apparatus (Waters) was equipped with 2 columns (pores diameter, 500 and 100 nm). The eluent used was tetrahydrofuran. Total epoxy conversion,  $x_T$ , is given by:

$$x_T = 1 - (h_t/h_0)^{0.5} \quad (3)$$

where  $h_t/h_0$  is the ratio of the peak height of epoxy monomer ( $n = 0$ ) at time  $t$ , with respect to the initial one.

## Results and Discussion

### Model System of Low Molar Mass

The model system was based on a DGEBA-EA mixture. Different formulations containing an excess of epoxy over

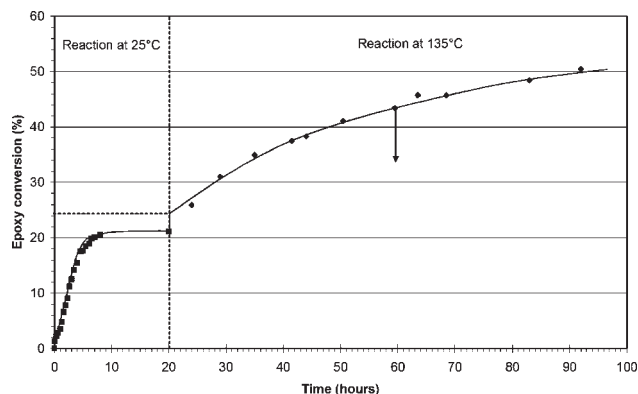


Figure 2. Evolution of the epoxy conversion for a DGEBA-EA solution with  $r=0.247$  (the arrow indicates gelation determined by the presence of an insoluble fraction in THF).

the stoichiometric value were selected (Table 1). The stoichiometry ratio,  $r$ , is the ratio between initial amine and epoxy groups ( $[NH]_0/[E]_0$ ).

Two different kinds of reactions may take place in these samples: a) the epoxy-aminohydrogen reaction, and b) the polyetherification of epoxy groups initiated by the tertiary amine generated in the first reaction. For the case of aliphatic amines, the first reaction is expected to proceed at a much faster rate than the second reaction.<sup>[12]</sup> Therefore, both reactions are expected to occur in series. As an example, Figure 2 shows the evolution of the epoxy conversion for the formulation with  $r=0.247$ .

The epoxy-amine reaction took place at 25 °C up to the vitrification, that occurred at an epoxy conversion close to 0.21. After 20 h at 25 °C, the sample was heated to 135 °C. During this heating period, the epoxy-amine reaction was presumably completed, reaching an epoxy conversion of 0.247. This first stage of the reaction between DGEBA and EA leads to a mixture of epoxy-terminated DGEBA-EA oligomers and residual DGEBA (Figure 3). This mixture is our model for the study of the second stage. After a short induction period, the polyetherification reaction took place

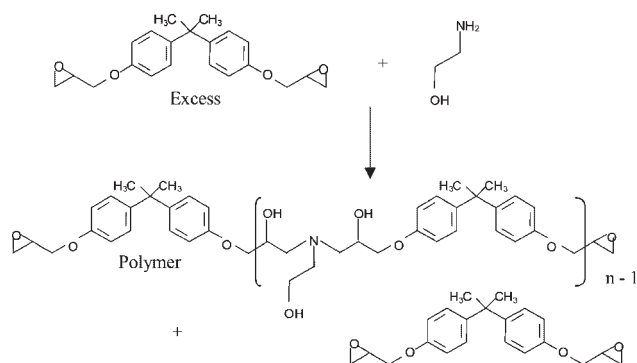


Figure 3. Reaction leading to our low molar mass model system for etherification studies.

at 135 °C, leading to gelation (lack of solubility in THF) at about 58 h (marked by an arrow).

After the complete reaction of EA, species present in the reaction mixture are unreacted DGEBA, a trimer composed of one EA and two DGEBA units, a pentamer composed of two EA and three DGEBA units, etc. This distribution may be determined by the Flory-Stockmayer statistics:<sup>[1]</sup>

$$N_n/[DGEBA]_0 = (1-r)^2 r^{(n-1)/2} \quad (n = 1, 3, 5, \dots) \quad (4)$$

where  $[DGEBA]_0$  is the initial number of moles of DGEBA and  $N_n$  indicates the number of moles of a generic species with  $n$  (DGEBA+EA) units in its chain. In particular, the fraction of unreacted DGEBA is equal to  $(1-r)^2$ , that corresponds to the simultaneous probability that both epoxy groups did not react.

The average molar masses may be calculated from the distribution given by Equation (4). The number-average molar mass ( $\bar{M}_n$ ) can be easily determined from the ratio between the total mass and the total number of moles. If the system is considered as a solution of an epoxy-amine linear polymer in DGEBA, the resulting  $\bar{M}_n$  of the polymer is a function of the initial stoichiometric ratio  $r$ :

$$\bar{M}_n (\text{kg} \cdot \text{kmol}^{-1}) = \frac{382.6 [1 - (1-r)^2] + 61r}{[(1 - (1-r)^2) - r]} \quad (5)$$

Table 2 shows concentrations after completion of the epoxy-amine reaction as well as the calculated  $\bar{M}_n$  of the generated polymer (excluding the residual DGEBA monomer).

The evolution of the epoxy conversion for formulations with different initial stoichiometric ratios, polymerized at 135 °C, is shown now in Figure 4.

Assuming that the polyetherification starts after completion of the epoxy-amine reaction during the initial period of the heating at 135 °C, the additional epoxy conversion related to polyetherification ( $x$ ), is given by:

$$x = (x_T - r)/(1 - r) \quad (6)$$

where  $x_T$  is the overall epoxy conversion (experimental points represented in Figure 4). A second-order kinetic

Table 2. Calculated concentrations of functional groups and number-average molar mass of the resulting polymer (excluding residual DGEBA), after completion of the epoxy-amine reaction.  $[N]_1$  is the concentration of tertiary amine after the epoxy-amine reaction.

$r$	$[E]_1$ mol · kg <sup>-1</sup>	$[OH]_1$ mol · kg <sup>-1</sup>	$[N]_1$ mol · kg <sup>-1</sup>	$\bar{M}_n$ kg · Kmol <sup>-1</sup>
0.247	3.787	2.243	0.621	972
0.328	3.338	2.817	0.815	1 043
0.481	2.520	3.865	1.168	1 237
0.658	1.618	5.024	1.556	1 680

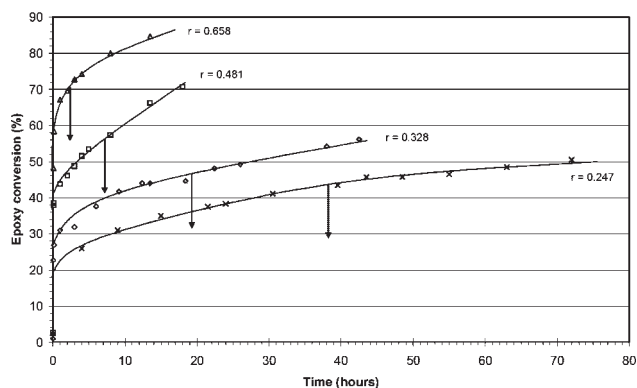
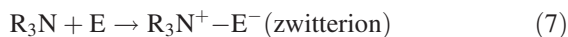


Figure 4. Evolution of the overall epoxy conversion,  $x_T$ , for DGEBA-EA mixtures with different initial stoichiometric ratios,  $r = [\text{NH}]_0/[\text{E}]_0$ , reacted at 135 °C (arrows indicate gelation).

model provided a very good fitting of kinetic curves, as shown in Figure 5.

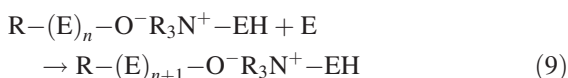
The polyetherification of epoxy groups proceeds through an anionic polymerization initiated by tertiary amines, in the presence of proton donor compounds.<sup>[13–19]</sup> The following mechanism may explain the observed second-order kinetics.

#### Initiation



where the alkoxide group constitutes the active initiator.

#### Propagation



#### Chain Transfer

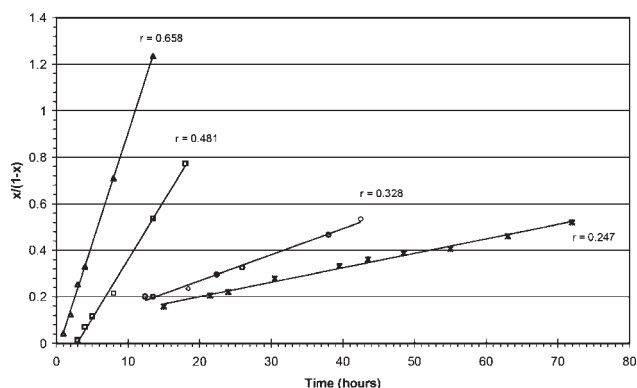
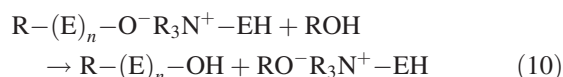
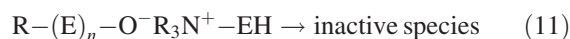


Figure 5. Second-order regression of the reaction kinetics at 135 °C, for DGEBA-EA mixtures with different initial stoichiometric ratios,  $r$ , after completion of the epoxy-amine reactions;  $x$  is the epoxy conversion during the etherification reaction.

#### Termination



The nature of inactive species formed in the termination step has been discussed in the literature.<sup>[13–15,17]</sup>

The rate of consumption of epoxy groups may be written as:

$$-d[\text{E}]/dt = k_p[\text{RO}^-][\text{E}] \quad (12)$$

Assuming a pseudo-steady state for the concentration of  $\text{RO}^-$ , leads to:

$$k_i[\text{N}]_1[\text{OH}]_1[\text{E}] = k_t[\text{RO}^-] \quad (13)$$

From Equation (12) and (13), the second-order rate Equation is obtained:

$$-d[\text{E}]/dt = (k_p k_i / k_t) [\text{N}]_1 [\text{OH}]_1 [\text{E}]^2 \quad (14)$$

Defining  $x = ([\text{E}]_1 - [\text{E}])/[\text{E}]_1$ , and integrating, leads to:

$$x/(1-x) = k t \quad (15)$$

where  $k = (k_p k_i / k_t) [\text{N}]_1 [\text{OH}]_1 [\text{E}]_1$ .

Values of  $k$  and  $(k_p k_i / k_t)$  for the different formulations are shown in Table 3.

The ratio of specific rate constants,  $k_p k_i / k_t$ , increases with the polarity of the solution, associated with the increase in the concentration of hydroxyl groups with  $r$ . Specific rate constants of anionic polymerizations vary with the polarity of the solvent mainly due to its effect on the separation of the active species and its counterion (quaternary ammonium in our case). An increase in polarity produces a larger separation of both ions, an effect that should act in increasing the propagation rate and decreasing the termination rate.

The gel conversion is determined by the interplay of two opposing effects associated with an increase in  $r$ . On one hand, an increase in  $r$  increases the average molar mass of the linear polymer formed after the first stage (reaction between oxirane and  $\text{NH}$ ) and, consequently, the number of functionalities where polymer chains may be initiated during the second stage. This effect produces a decrease in the gel conversion by increasing  $r$ . On the other hand, an increase in the concentration of  $\text{OH}$  groups increases the

Table 3. Regression coefficients of the second-order kinetics ( $R$ ), specific rate constants and gel conversions,  $x_{\text{gel}}$ , for the polyetherification reaction (second stage of the reaction) of DGEBA-EA formulations at 135 °C, for different stoichiometric ratios;  $x_{T\text{gel}}$  is the measured overall gel conversion.

$r$	$R$	$k$ $\text{h}^{-1}$	$k_p k_i / k_t$ $\text{kg}^3 \cdot \text{mol}^{-3} \cdot \text{h}^{-1}$	$x_{\text{gel}}$	$x_{T\text{gel}}$
0.247	0.9909	$6.250 \times 10^{-3}$	$1.185 \times 10^{-3}$	0.247	0.43
0.328	0.9922	$1.163 \times 10^{-2}$	$1.518 \times 10^{-3}$	0.208	0.47
0.481	0.9974	$5.044 \times 10^{-2}$	$4.434 \times 10^{-3}$	0.172	0.57
0.658	0.9997	$9.549 \times 10^{-2}$	$7.550 \times 10^{-3}$	0.158	0.71

rate of chain transfer leading to a decrease in the average length of the polyether chain formed by propagation steps. Experimental results shown in Table 3 indicate that the gel conversion in the polyetherification reaction decreases by increasing the stoichiometric ratio  $r$ . This is ascribed to the increase in the average number of OH groups per linear polymer chain that are available to initiate polyether chains in the crosslinking reaction

### Crosslinkable Thermoplastic Blends

When DGEBA-BLOX formulations are prepared, epoxy-amine reactions involving the AEEA stabilizer and chain ends of BLOX occur first during blending, well before the start of polyetherification. BLOX macromolecules have one NH groups at each end. But as AEEA has three NH groups, a premature gel might be produced by the epoxy-amine reaction below a critical DGEBA excess (above a critical BLOX mass fraction). The gel conversion in the epoxy-amine polymerization may be calculated from:<sup>[1]</sup>

$$(x_e x_a)_{\text{gel}} = 1 / [(f_e - 1)(g_e - 1)] \quad (16)$$

where  $x_e$  and  $x_a$  are, respectively, the conversions of epoxy and amine functionalities, and  $f_e$  and  $g_e$  are the functionality-average functionalities of epoxy and amine monomers, defined by:<sup>[1]</sup>

$$f_e = \sum f_i^2 A_i / \sum f_i A_i \quad \text{and} \quad g_e = \sum g_i^2 B_i / \sum g_i B_i \quad (17)$$

where  $A_i$  and  $B_i$  represent the number of moles of epoxy and amine monomers, with functionalities  $f_i$  and  $g_i$ .

As every epoxy monomer is bifunctional,  $f_e = 2$ . On the other hand, BLOX contains 0.5 wt.-% of AEEA. This leads to 0.6378 moles of AEEA per mole of BLOX, giving  $g_e = 2.489$ . For a formulation containing an epoxy excess,  $r$  (amine equivalents/epoxy equivalents)  $< 1$ , when  $x_a = 1$ ,  $x_e = r$ . From Equation (16), the critical gelation ratio is given by:

$$r_c = 1 / 1.489 = 0.6716 \quad (18)$$

A formulation with  $r < r_c$  will not gel at the end of the epoxy-amine reaction, which means that it can be processed like a thermoplastic with the help of an extruder during the first reaction stage. This corresponds to a BLOX mass fraction of 94.1 wt.-% (including the AEEA stabilizer) in a mixture with DGEBA. Blends containing lower mass fractions of BLOX will not gel after completion of the epoxy-amine reaction. Selected formulations for this study had 16, 30, 50 and 70 wt.-% BLOX in the mixture with DGEBA.

Table 4 shows the concentrations of different functional groups, calculated after completion of the epoxy-amine reaction, for formulations containing different BLOX amounts.

Table 4. Concentration of different functional groups after completion of the epoxy-amine reaction, for DGEBA-BLOX formulations.

BLOX wt.-%	$[E]_1$ $\text{mol} \cdot \text{kg}^{-1}$	$[\text{OH}]_1$ $\text{mol} \cdot \text{kg}^{-1}$	$[N]_1$ $\text{mol} \cdot \text{kg}^{-1}$
16	4.344	1.582	0.423
30	3.571	2.623	0.792
50	2.466	4.110	1.321
70	1.362	5.597	1.849

DGEBA-BLOX formulations were polymerized at 135 °C and the epoxy conversion was followed as a function of time (Figure 6). Arrows indicate the gel times of the different systems. The conversion in the etherification reaction,  $x$ , (second stage of the reaction) was calculated using Equation (6), and the results were regressed using a second-order kinetics. A good fitting was obtained, as illustrated in Figure 7. Kinetic constants and times to gel of the different blends, are reported in Table 5.

Polyetherification rates exhibit the same trend as in DGEBA-EA formulations. There is a significant increase of

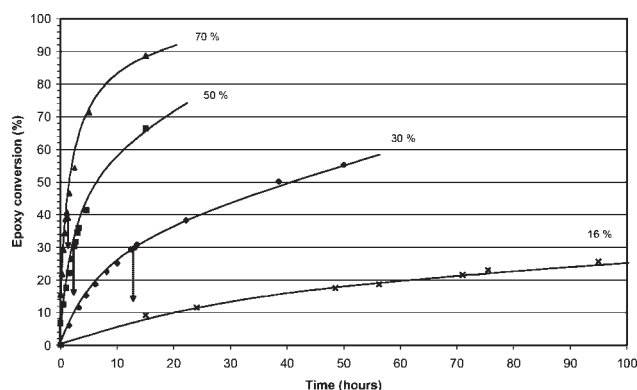


Figure 6. Evolution of the overall epoxy conversion for DGEBA-BLOX blends with different mass fractions of BLOX, reacted at 135 °C (arrows indicate gelation).

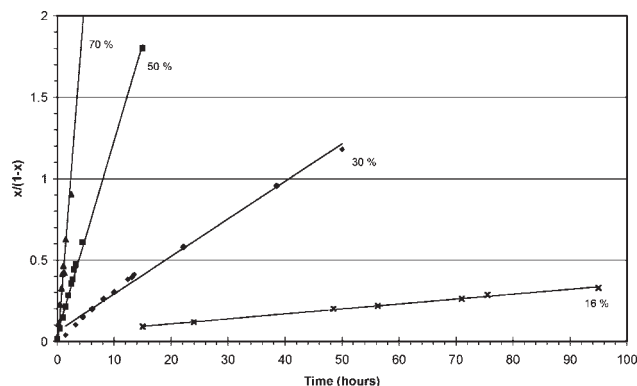


Figure 7. Second-order regression of the polyetherification kinetics at 135 °C, for DGEBA-BLOX formulations with different BLOX mass fractions.

Table 5. Regression coefficients of the second-order kinetics ( $R$ ), specific rate constants and gel conversions, for the polyetherification reaction of DGEBA-BLOX formulations at 135 °C, for different blend compositions;  $t_{\text{gel}}$  is the experimental gel time.

BLOX wt.-%	$R$	$k$ $\text{h}^{-1}$	$k_{\text{p}}k_{\text{i}}/k_{\text{t}}$ $\text{kg}^3 \cdot \text{mol}^{-3} \cdot \text{h}^{-1}$	$x_{\text{gel}}$	$t_{\text{gel}}$
16	0.9980	$3.040 \times 10^{-3}$	$1.05 \times 10^{-3}$	0.364	144 h
30	0.9964	$2.309 \times 10^{-2}$	$3.11 \times 10^{-3}$	0.282	13 h 15 min
50	0.9987	$1.176 \times 10^{-1}$	$8.78 \times 10^{-3}$	0.262	2 h 30 min
70	0.9991	$4.416 \times 10^{-1}$	$31.33 \times 10^{-3}$	0.294	1 h

the polymerization rate when increasing the polarity of the medium by the BLOX addition. The apparent rate constant, ( $k_{\text{p}}k_{\text{i}}/k_{\text{t}}$ ), lies in the same order than the one determined for DGEBA-EA solutions, up to a BLOX mass fraction of 50%. However, the formulation containing 70 wt.-% BLOX shows a significantly higher polyetherification rate, a fact that may be useful for post-crosslinking purposes.

Due to the competition between the increase in both the concentration of polyfunctional chains and the rate of chain transfer steps, when increasing the amount of BLOX in the blend, the gel conversion did not vary significantly for formulations containing from 30 to 70 wt.-% BLOX. However, for BLOX amounts close to 94 wt.-% it is expected that gelation takes place after completion of the epoxy-amine reaction, i.e.,  $x_{\text{gel}} = 0$ . Therefore a significant decrease in the gel conversion should be evidenced for BLOX amounts close to this critical value.

## Conclusion

Poly(hydroxyl-amino ethers) based on DGEBA and ethanol amine monomers are new linear thermoplastic polymers containing one primary hydroxyl groups, two secondary hydroxyl groups and one tertiary amino groups per repeating unit. They also contain one secondary amino group at both ends, and a few percent of aminoethyl ethanol amine as "stabilizer". When these thermoplastic polymers are blended with liquid DGEBA for processing reasons, two stages of reactions are expected to occur, i) epoxy-aminohydrogen reactions, and ii) epoxy homopolymerization initiated by tertiary amines.

The two stages have been studied first using a low molar mass model system, and then with the polymer blend. As expected the first reaction is very fast and occurs during blending at low temperatures. This reaction does not lead to a gel if the amount of TP stabilizer is low. Blends with more than 6 wt.-% of DGEBA were processable without any problem derived from gelation.

The second reaction occurred during a post-cure and transformed the TP blend into a crosslinked polymer. Du-

ring curing at 135 °C the gel time depended on the blend composition, from 1 h for 70 wt.-% TP to 140 h for 16 wt.-% TP. The polyetherification rate followed a second-order kinetic equation.

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