

Polymerization of an Epoxy Resin Modified with Azobenzene Groups Monitored by Near-Infrared Spectroscopy

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ABSTRACT: New photosensitive materials containing photochromic azobenzene moieties were synthesized. For this purpose, an epoxy resin based on diglycidyl ether of bisphenol A (DGEBA) was reacted with an azobenzene chromophore (disperse orange 3, AZ) to satisfactorily synthesize an azo-modified prepolymer, which was then used to generate series of epoxy-based polymers containing azo groups. Three different amines were used as hardeners, with the aim of obtaining materials with different chemical structures. Understanding the epoxy resin polymerization kinetics is essential for intelligent processing of materials. Near-IR (NIR) spectral analysis was used to follow the polymerization kinetics. The quality of the NIR

spectra enables concentrations of individual chemical species to be measured in real time. Conversion of epoxy and primary amine groups, as well as the concentration of different groups, as a function of reaction time was therefore calculated by this spectroscopic technique. Samples containing azo units were compared to the pure DGEBA/amine systems. Results showed that the azo-prepolymer incorporation has an accelerating effect on polymerization rate. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 112: 2999–3006, 2009

Key words: azobenzene chromophore; epoxy; kinetics; near-infrared spectroscopy

INTRODUCTION

The need for materials better suited for emerging technological applications has prompted the study of new polymers. Thermoset epoxy composites are most often used in high-performance applications because of their unique properties, which result in a wide range of applications. In this respect, the preparation of epoxy systems containing azobenzene moieties appears to be very promising. Indeed, the photoinduced *trans-cis-trans* isomerization of azobenzene chromophores can give rise to photochromic and optical dichroic effects.^{1–13} These properties are attracting increasing attention because of their potential applications in optical information storage, optical switching devices, diffractive optical elements, and other areas.^{14–18}

The curing kinetics of epoxy resins with amines has been well investigated in the past. There are three basic reactions occurring during curing: (1) the epoxy group reacts with a primary amine to produce a secondary amine, (2) the epoxy group reacts with a secondary amine to produce a tertiary amine, and (3) secondary reactions, such as etherification and homopolymerization of the epoxy group, resulting in the formation of an ether link.

Near-IR (NIR) spectroscopy was chosen to *in situ* monitoring the reactions because its ability to quantitatively follow the concentration changes of different functional groups in epoxy/amine systems is well documented.^{19–25} Fourier transform infrared studies, in either mid-IR or NIR regions, can generate both overall reaction kinetics and also the reaction rates of each single reaction through the monitoring of the intensity changes of the corresponding bands of different functional groups. Nevertheless, the complex nature of mid-IR spectra and the overlapping bands make it a difficult technique to use. NIR spectroscopy, however, is a powerful tool because of its relative simplicity in comparison with mid-IR spectroscopy. The NIR region encompasses bands that result from the harmonic overtones of fundamental and combination bands associated with hydrogen atoms, which is why compounds containing O–H,

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TABLE I
Chemical Structures of the Used Reactants

Symbol	Structure
DGEBA	
AZ	
BA	
MT	
MXDA	

N—H, and/or C—H bonds lend themselves favorably to analysis by NIR.

The main objective of this work is to *in situ* monitoring the reaction of azobenzene-modified epoxy polymers by NIR, with the aim of developing new materials that could be used in the area of photonics and electronics. In previous experiments of photoinduced anisotropy,¹³ we found that these polymers are actually promising materials to be employed in those technological areas. We studied the phenomenon of perpendicular orientation of the azobenzene groups to the polarized light of a laser beam and, in a subsequent paper, a deep analysis of the optical behavior of this azo-modified polymers will be presented.

EXPERIMENTAL

Materials

A bifunctional epoxy resin, diglycidyl ether of bisphenol A (DGEBA, DER 332, $n = 0.03$), with an epoxy equivalent of 174 g eq^{-1} was gently provided by Dow Chemical. Benzylamine (BA), *m*-toluidine (MT), *m*-xylylenediamine (MXDA), and the azobenzene chromophore (4-(4-nitrophenylazo)aniline, disperse orange 3, with a melting temperature of 200°C) (AZ) were supplied by Aldrich. Their chemical structures are shown in Table I.

Samples preparation

An azo-prepolymer (TAZ) was synthesized by reaction between DGEBA and AZ by a procedure previously described.¹³ It was prepared in a stoichiometric ratio $r = \text{AZ eq}/\text{DGEBA eq} = 0.5$ to achieve a reaction product with epoxy groups in the end of chains. The sample was prepared mixing DGEBA and the required amount of AZ at 200°C , in an oil bath during 2 min to obtain a homogeneous solution. Then, reaction was carried out in an oil bath at 180°C during 58 min. The resulting TAZ was blended with DGEBA and two different monoamines (MA), one aliphatic (BA) or one aromatic (MT), to prepare azo-modified thermoplastics. Reagents were mixed at room temperature adding some tetrahydrofuran (THF) drops to homogenize the samples. After that, THF was removed by evaporation at room temperature. Polymerization reactions were carried out at 60°C for BA and at 100°C for MT. Along with the MA, an aliphatic diamine (MXDA) was used as hardener with the aim of developing a crosslinked polymer. In this case, reaction was carried out at 100°C .

Technique

Fourier transform infrared spectroscopy was performed using a Nicolet Nexus 670/870 Spectrometer. NIR data were obtained using a calcium fluoride beam splitter, a white light source, and a MCT/A detector cooled with liquid nitrogen. All spectra were generated at 8 cm^{-1} resolution using 36 scans. A large core ($600/630 \mu\text{m}$) low O—H fused silica-type multimode optical fiber (3M's specialty optical fiber) was used. The fiber was characterized by an attenuation at 630 nm ($15,000 \text{ cm}^{-1}$) of less than 50 dB/km , and a numerical aperture of 0.39 ± 0.02 . Two fibers were used as received, and transmitting legs SMA (SMART) connectors (supplied by Newark Electronics) were used to attach fiber legs to the fiber link. A short length (less than 10 mm) of the protective buffer was removed from the distal ends of fibers, which were then slipped into the capillary to the desired path length. The space between fiber ends was filled with the reactive mixture, and the whole assembly was inserted into an oil bath at the required temperature.

RESULTS AND DISCUSSION

NIR data were collected in a remote optical fiber assembly during the polymerization of different epoxy/amine systems. The assignment of relevant peaks in epoxy/amine reaction is listed in Table II. The evolution in NIR spectra of an AZ/DGEBA formulation with $r = 0.5$, during reaction at 180°C at

TABLE II
NIR Assignments of the Relevant Peaks in Epoxy/Amine Reactions

Wavenumber (cm ⁻¹)	Peak assignment
4530	Epoxy combination peak (stretching and bending vibrations)
4623	—CH stretching vibration due to benzene ring
4800–4900	Hydroxyl combination peak
4947–5078	Primary amine combination peak (stretching and bending vibrations)
6080	Epoxy stretching vibration (first overtone)
6530–6687	Primary and secondary amine stretching vibration
7000	Hydroxyl stretching vibration (first overtone)

various times, was shown in a previous article.¹³ The trends displayed by the major peaks of relevance in epoxy/amine systems were evident: a progressive decrease in epoxy absorption (4530 and 6080 cm⁻¹) during reaction; a decrease in amine absorption (5078 and 6687 cm⁻¹), indicating that the primary amine reacted with epoxy to be converted in a secondary amine, and an increase in hydroxyl absorption (7000 cm⁻¹), confirming that condensation took place.

Epoxy and primary amine groups conversions at any time t were calculated from the initial areas of peaks at 4530 cm⁻¹, $A_{EP,0}$, and 5078 cm⁻¹, $A_{PA,0}$, with respect to the area of the reference peak at 4623 cm⁻¹, $A_{ref,0}$, and their corresponding values at time t , $A_{EP,t}$, $A_{PA,t}$, and $A_{ref,t}$, according to the following equation:

$$X = 1 - [(A_t)(A_{ref,0})]/[(A_0)(A_{ref,t})] \quad (1)$$

Conversion versus time curves obtained for epoxy and primary amine groups were also shown in a previous work.¹³ To determine whether DGEBA and AZ were reacted during mixing, a NIR spectrum of DGEBA at 180°C was carried out. It was considered that the area of the peak at 4530 cm⁻¹ of pure DGEBA spectrum corresponded to epoxy conversion (X_{EP}) = 0. According to this, it was determined that at the beginning of the kinetic study (0 min), the epoxy conversion was 0.16. The primary amine was completely converted in secondary amine after ~ 50 min. In addition, the epoxy conversion after the same period was around 0.50.

The epoxy $[EP]_t$ and primary amine $[PA]_t$ concentrations at time t can be calculated with the following equations:

$$[EP]_t = [EP]_0(1 - X_{EP}) \quad (2)$$

$$[PA]_t = [PA]_0(1 - X_{PA}) \quad (3)$$

where $[EP]_0$ and $[PA]_0$ are the epoxy and primary amine groups concentrations at time 0, respectively; and X_{PA} , the primary amine groups conversion at time t .

With respect to the secondary amine group concentration at time t , $[SA]_t$, both primary and secondary amines do absorb at 6687 cm⁻¹, this peak cannot be directly used to follow the secondary amine group evolution. To solve this problem, a method, previously proposed by Schlup and coworkers,¹⁹ can be followed as long as the contribution of secondary reactions will not be significant. Etherification reactions become important only at high temperature (above 150°C), especially when high epoxy/amine ratios are used.²⁰ Regarding the homopolymerization reaction, it is considered that occurs only at high temperature, being initiated by specific catalysts such as Lewis acids, tertiary amines, impurities, and so on.¹⁹ Furthermore, such reaction usually does not take place when aromatic amines are used as curing agents, because the tertiary amines formed are sterically hindered.²⁶ In any case, in etherification like in homopolymerization reactions, an ether linkage is formed and there is no change in number of hydroxyl groups.

AZ/DGEBA, $r = 0.5$, reaction was carried out at high temperature (180°C) and, in addition, this formulation has an epoxy excess. Therefore, these experimental conditions might contribute to the existence of etherification reactions. On the other hand, etherification reactions are unlikely to occur in the rest of the studied systems, because stoichiometric amounts of epoxy and amine were used, and polymerization reactions were carried out at low temperatures (60 and 100°C). Thus, in the case in which the contribution of etherification reaction is negligible, the sum of epoxy and hydroxyl groups concentrations keeps constant, and the concentrations of secondary and tertiary amine, $[TA]_t$, can be obtained from the following mass balances:

- (a) Nitrogen balance (the total number of nitrogen atoms remain constant),

$$[PA]_t + [SA]_t + [TA]_t = [PA]_0 \quad (4)$$

- (b) Hydroxyl group (OH) balance,

$$[SA]_t + 2[TA]_t = [OH]_t \quad (5)$$

In the absence of etherification reactions,

$$[EP]_0 - [EP]_t = [OH]_t \quad (6)$$

If etherification reactions cannot be neglected, the excess of epoxy groups will be consumed to form ether linkages, that is

$$[EP]_0 - [EP]_t = [OH]_t + [ET]_t \quad (7)$$

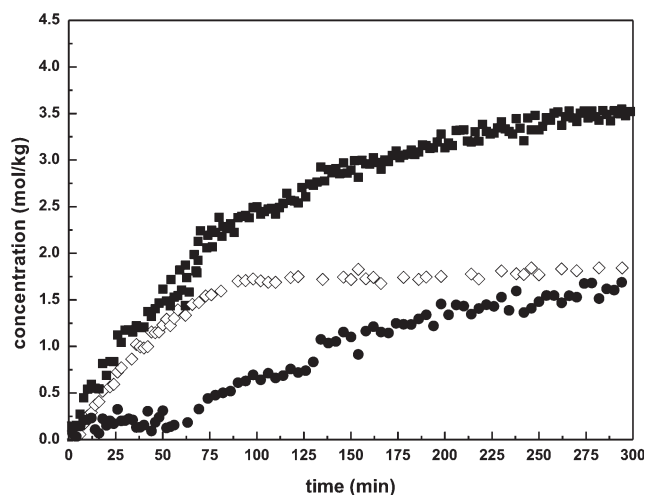


Figure 1 Evolution of epoxy ($[\text{EP}]_0 - [\text{EP}]_t$) (■), ether (●), and hydroxyl (◇) groups concentration as a function of time for an AZ/DGEBA mixture, $r = 0.5$, reacted at 180°C .

where $[\text{ET}]_t$ denotes the concentration of ether linkages.

By means of the above expressions, it is possible to obtain the following equations:

$$[\text{SA}]_t = 2([\text{PA}]_0 - [\text{PA}]_t) - ([\text{EP}]_0 - [\text{EP}]_t) \quad (8)$$

$$[\text{TA}]_t = [\text{PA}]_0 - [\text{PA}]_t - [\text{SA}]_t \quad (9)$$

Before using this method, it is necessary to verify whether or not etherification reaction occurs through polymerization reactions. With this purpose, a method previously reported by St. John and George²¹ was used. This method consists of calculating the secondary amine concentration with the integrated area at 6687 cm^{-1} (A), where primary amine overtone bands overlap with secondary amine overtone bands. If Beer's law is followed and e_1 and e_2 are the extinction coefficients for the primary and secondary amines, then

$$A = e_1[\text{PA}]_t + e_2[\text{SA}]_t \quad (10)$$

In the first few minutes of reaction, it is generally safe to assume that no secondary amine reaction or etherification occurs. Thus, the secondary amine concentration can be calculated with eq. (11), because the consumption of primary amine would only produce secondary amine:

$$[\text{SA}]_t = [\text{PA}]_0 - [\text{PA}]_t \quad (11)$$

With the set of concentration data ($[\text{PA}]_t$ and $[\text{SA}]_t$) and the set of total area (A) values [eq. (10)] integrated from the spectra obtained within the first minutes of reaction, best fitted values for e_1 and e_2 can be found through the solution of equations with

two variables. The secondary amine concentration at any time t can then be calculated with

$$[\text{SA}]_t = (A - e_1[\text{PA}]_t)/e_2 \quad (12)$$

The concentrations of tertiary amine groups [eq. (9)] and hydroxyl groups [eq. (5)] were calculated with the values of $[\text{SA}]_t$ obtained from eq. (12), verifying first the presence or not of etherification reactions with eq. (7), to consequently apply the method based on the mass balances. If etherification reaction did not occur, the number of epoxy groups consumed during cure should be equal to the number of hydroxyl groups formed. Otherwise, additional consumption of epoxy, equal to the number of ether links formed, must be observed.

As can be seen in Figure 1, where the changes in epoxy, ether, and hydroxyl groups concentrations are plotted, the etherification contribution is significant during AZ/DGEBA, $r = 0.5$, reaction in the used conditions. Moreover, as Figure 2 shows the continuous decrease in intensity of the epoxy absorption band after depletion of the secondary amine groups is a clear indication that etherification reaction occurred in this system. Therefore, the concentrations of secondary and tertiary amines were calculated from the overlapping overtone band at 6687 cm^{-1} as suggested by St. John and George.²¹ Figure 3 shows the concentration changes of the different functional groups during reaction of AZ/DGEBA, $r = 0.5$, system. The primary amine completely disappeared after ~ 50 min. The secondary amine concentration increased from the beginning of reactions and it reached the maximum after around 25 min. Because etherification reaction does not contribute to the global change in hydroxyl concentration, both hydroxyl and tertiary amine

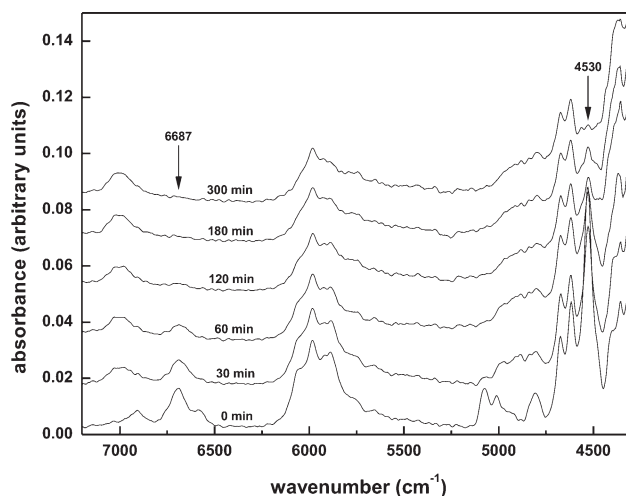


Figure 2 NIR spectra of an AZ/DGEBA mixture, $r = 0.5$, during reaction at 180°C for total time = 300 min.

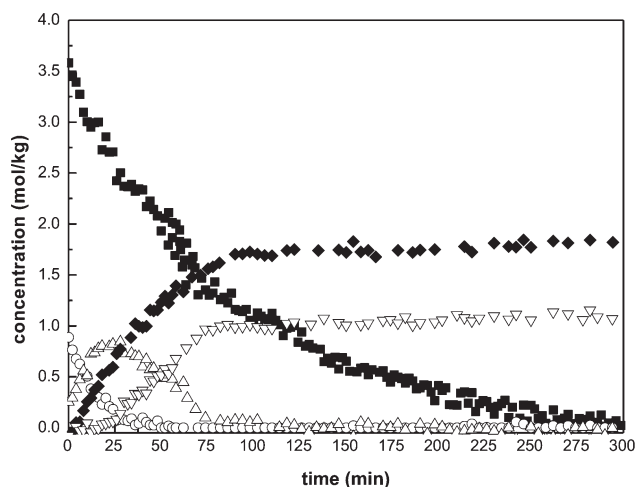


Figure 3 Evolution of epoxy (■), hydroxyl (◆), primary (○), secondary (△), and tertiary amine (▽) groups concentration as a function of time for an AZ/DGEBA mixture, $r = 0.5$, reacted at 180°C .

concentrations remained constant after the complete reaction of the secondary amine groups.

Based on this knowledge, to prepare final materials, 58 min was selected as polymerization time with the purpose of obtaining a prepolymer (TAZ) that subsequently could be dissolved in epoxy/amine mixtures, avoiding etherification reaction. Therefore, the resulting TAZ was blended with two different MA, BA and MT, and DGEBA. Samples were prepared with 20 wt % TAZ (TAZ20) (i.e., 5.16 wt % of AZ) and DGEBA was added in the necessary amount to obtain a stoichiometric ratio $r' = \text{epoxy (TAZ + DGEBA) eq/amine (MA) eq} = 1$, considering the unreacted epoxy groups in TAZ and that all the initial primary amine equivalents in TAZ were consumed after 58 min of reaction. TAZ was also blended in a similar way with a diamine (MXDA) to obtain a crosslinked azo-modified polymer.

Figure 4(a–c) shows a series of spectra recorded at various reaction times during TAZ20/DGEBA/BA, TAZ20/DGEBA/MT, and TAZ20/DGEBA/MXDA polymerization, respectively. For all the systems, it was verified that the epoxy conversion was 0 at the beginning of the kinetic study. Conversion versus time curves were obtained in a similar manner than for the TAZ synthesis. Figure 5(a–c) compares epoxy and primary amine groups conversion for systems containing TAZ and for the neat systems. In all systems, reaction rate increased with TAZ addition. According to Figure 3, during reaction of AZ/DGEBA, $r = 0.5$, system, the secondary amine group concentration was around 0.4 mol/kg after ~ 58 min, which means that TAZ had secondary amine groups in its chemical structure. In particular, approximately, half of the secondary amine groups had converted into tertiary amine groups. As r' was

calculated supposing that TAZ only had tertiary amine groups, its real value would be around 1.03 instead of 1. This amine excess could be a reason why polymerization rate increased with TAZ addition.

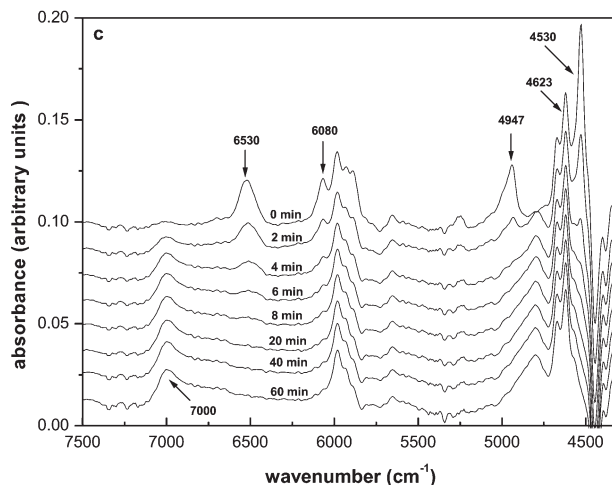
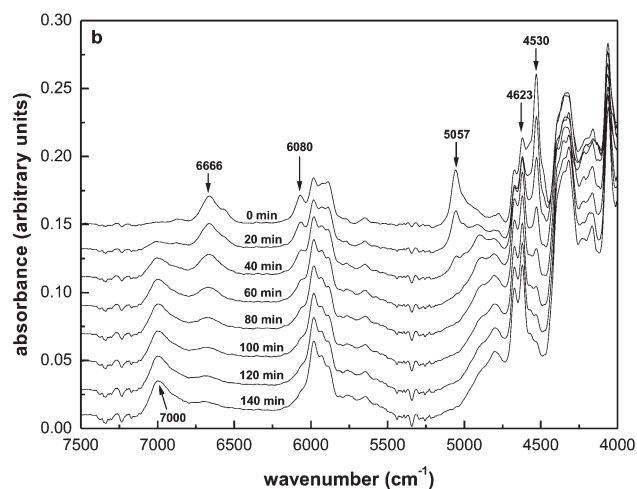
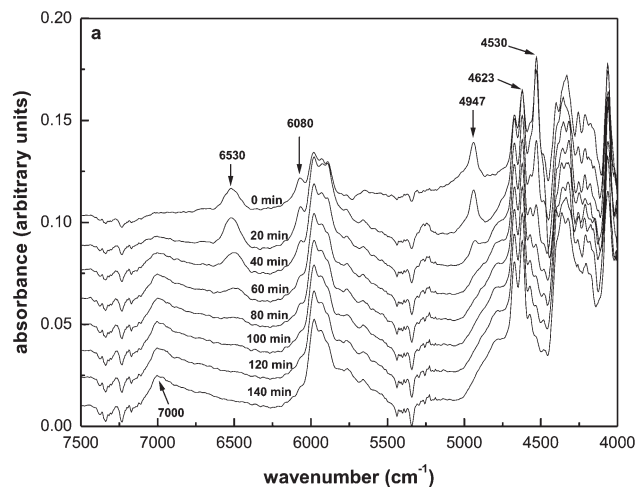


Figure 4 NIR spectra of a TAZ20/DGEBA formulation during reaction with: (a) BA, 60°C ; (b) MT, 100°C ; and (c) MXDA, 100°C .

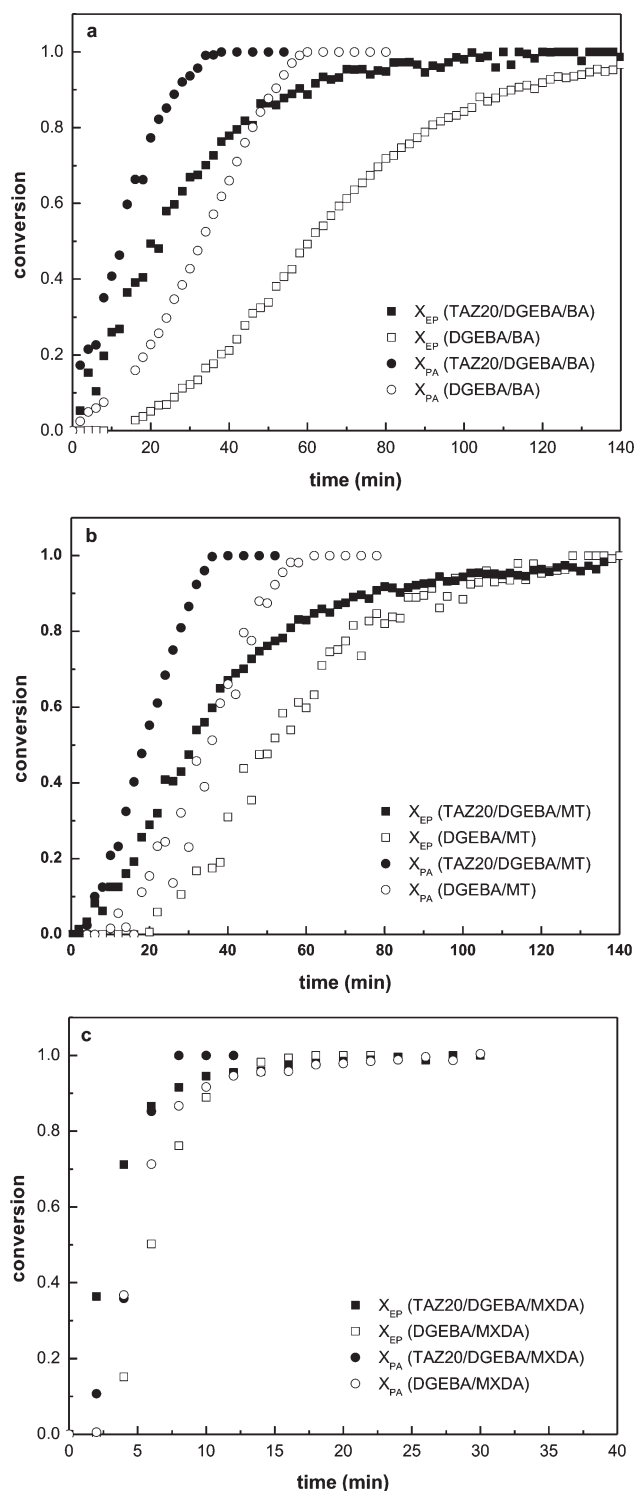


Figure 5 Epoxy (X_{EP}) and primary amine (X_{PA}) conversion as a function of reaction time for DGEBA and TAZ20/DGEBA formulations during reaction with: (a) BA, 60°C; (b) MT, 100°C; and (c) MXDA, 100°C.

In Figure 6, the evolution of concentration of the different groups (epoxy, ether, hydroxyl) for TAZ20/DGEBA/BA system clearly shows that etherification reaction was not observed during the course of reaction for this system. Similar results

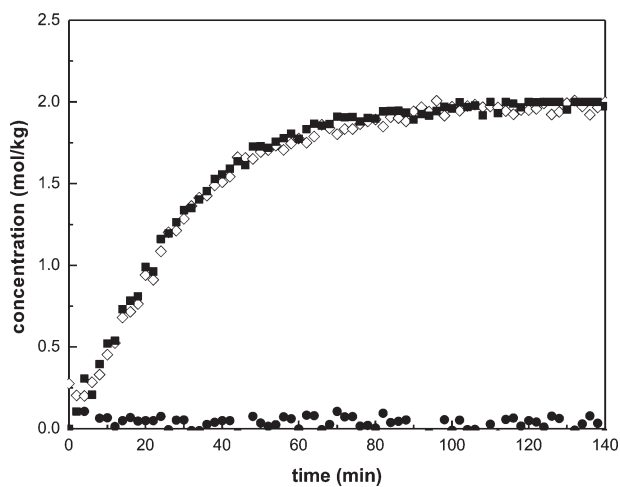


Figure 6 Evolution of epoxy ($[EP]_0 - [EP]_t$) (■), ether (●), and hydroxyl (◇) groups concentration as a function of time for a TAZ20/DGEBA/BA formulation during reaction at 60°C.

were obtained for TAZ20/DGEBA/MT and TAZ20/DGEBA/MXDA systems. Therefore, the concentrations of secondary and tertiary amines could be directly determined following the mass balance equations. But, first, it was compared the secondary amine concentration determined from the overlapping overtones bands from 6530 to 6666 cm^{-1} and by the method of the mass balances. As illustrated in Figure 7, the evolution of the secondary amine concentration for TAZ20/DGEBA/BA system during reactions obtained from both methods agreed well, which confirmed the validity of the mass balance method. In the same way, similar results were obtained for TAZ20/DGEBA/MT and TAZ20/DGEBA/MXDA systems. Thus, typical concentration profiles obtained from the mass balance equations

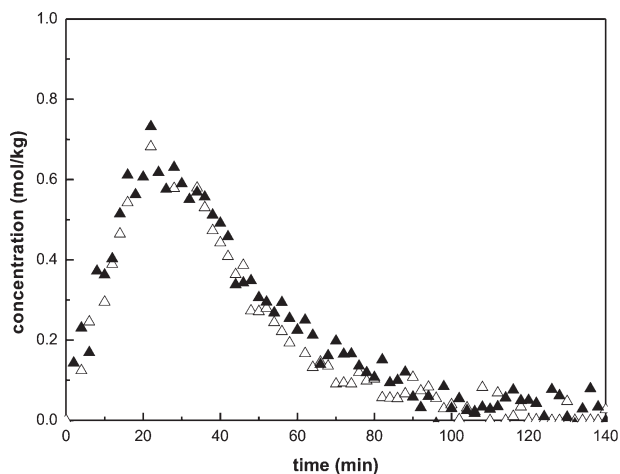


Figure 7 Evolution of secondary amine group concentration obtained from the mass balances (Δ) and from the overlapping overtone band (\blacktriangle) for a TAZ20/DGEBA/BA formulation during reaction at 60°C.

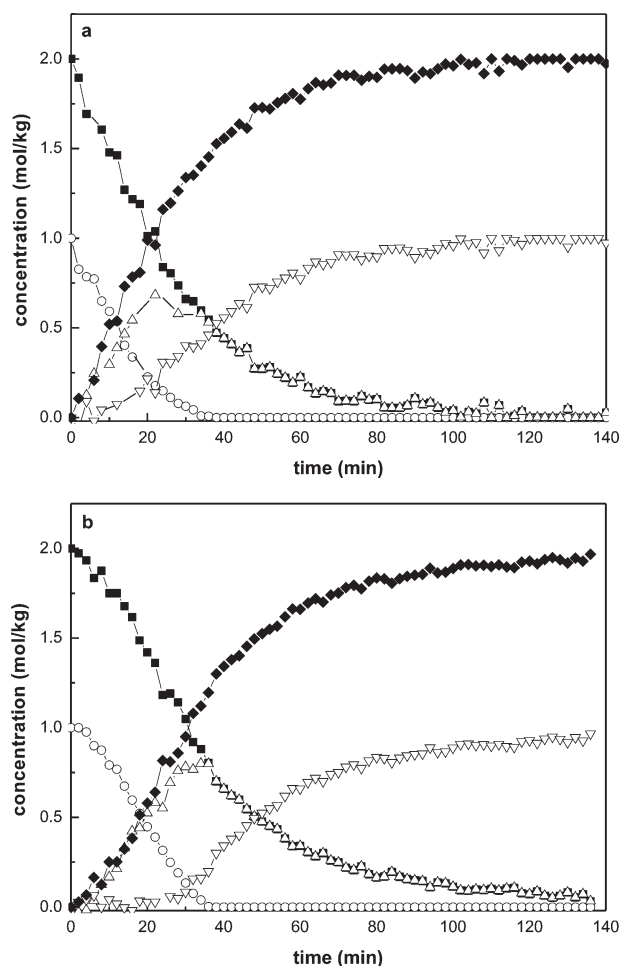


Figure 8 Evolution of epoxy (■), hydroxyl (◆), primary (○), secondary (△), and tertiary amine (▽) groups concentration as a function of time for a TAZ20/DGEBBA formulation during reaction with: (a) BA, 60°C and (b) MT, 100°C.

for the linear systems during reactions are plotted in Figure 8(a,b). In both cases, epoxy groups showed major trends to react with primary amines, whose concentration quickly decreased. Secondary amine concentration increased at the beginning of reactions, but the maximum was reached before the total disappearance of primary amines and tertiary ones also appeared before all the primary amine was converted in secondary. In the system with BA, the maximum of secondary amine concentration was reached after ~ 22 min and in the case of MT, after ~ 30 min; whereas primary amines completely disappeared after around 34 and 36 min, respectively. As soon as all primary amine groups had reacted, the secondary ones and epoxy groups evolved in a similar way. Moreover, the evolution of hydroxyl groups was parallel to that of epoxy ones, because of the fact that the first ones arose from the reaction of the second ones. In the case of the system with MXDA, the kinetic study was followed at 100°C to

obtain total conversion of the reactants. At that temperature, the polymerization rate was so high that made difficult the monitoring of the evolution of the different groups as a function of cure time. In consequence, a clear plot for these data was not possible to determine. Despite that fact, the kinetics study was carried out to corroborate that such accelerating effect on polymerization rate with TAZ incorporation also took place for this thermoset system.

CONCLUSIONS

It is worth mentioning that there is an increasing interest in polymers containing substituted azobenzene units, because of their potential nonlinear optical properties. In this study, series of azo-polymers based on an epoxy resin were synthesized. The reaction kinetics of the different azo-modified systems were investigated. The evolution of epoxy and primary amine conversions with reaction time was recorded using NIR spectroscopy. The concentration of epoxy, hydroxyl, primary, secondary, and tertiary amine groups as a function of reaction time was also calculated. Two methods were used for the analysis of the secondary amine groups and it was verified that both agreed well.

Experimental data showed that etherification reactions only occurred in the system having double equivalents of epoxy than equivalents of amine, and in which polymerization was carried out at high temperature (180°C).

Results also indicated that the addition of the azo-prepolymer accelerated the epoxy/amine reaction rate for all the analyzed systems probably because of the amine excess provided by secondary amine groups in its chemical structure (which implied the preparation of formulations slightly rich in amine), as polymerization rate is directly proportional to the amine initial concentration.

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