

Curing of Dicyandiamide Epoxy Resins Accelerated with Substituted Ureas

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ABSTRACT: An epoxy resin based on bisphenol-A-diglycidylether (DGEBA) was cured with dicyandiamide (DDA) and different substituted ureas (Urones) as accelerators. Differential scanning calorimetry, size exclusion chromatography, and Fourier transform infrared (IR) analysis indicated complex reaction mechanisms. The DDA granulometry seemed not to be a predominant parameter, but its content clearly influences T_g of the network. The maximum T_g value was found for an amine-to-epoxy molar ratio of 0.6. IR spectra revealed the appearance of oxazolidone rings, which are the first product of epoxy reactions. Urone accelerators also acted as homopolymerization initiators; they modified the epoxy conversion at gelation and changed of the structure of the obtained network. Influence of uron nature and content on reaction rates were also studied. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* 69: 2487–2497, 1998

Key words: urones; dicyandiamide; epoxy conversion

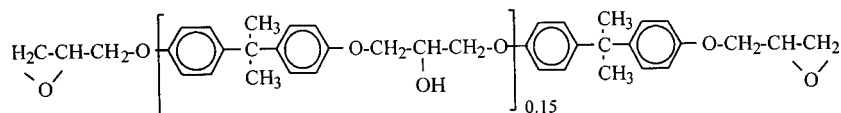
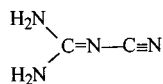
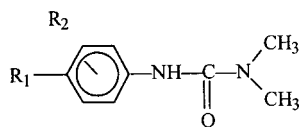
INTRODUCTION

Dicyandiamide (DDA) is widely used as a latent curing agent in epoxy resins and for prepregs application. Many studies have been devoted to the understanding of the reaction mechanisms and the structure–properties relationships.^{1–7} All these studies did not enable a precise mechanism to be established. Moreover, some authors concluded that the DDA functionality was not equal to 4, and other different functionality values were proposed.^{3,8} DDA is a solid powder characterized by very poor solubility in epoxy resins.⁹ Using urones as accelerators reduces the curing temperature and preserves the latency necessary to formulate vinyl–component systems.⁸ Upon heating, urones dissociate into isocyanate and dimeth-

ylamine.⁸ Dimethylamine reacts with an epoxy group to give a tertiary amine,^{10,11} which catalyzes the reaction of DDA with epoxy groups. The isocyanate reacts with another epoxy unit, forming an 1,3-oxazolidin-2-one,^{8,10–12} characterized by a Fourier transform mid-infrared (FTMIR) peak^{12,13} at 1760 cm^{-1} . A recent investigation showed that the addition of any amount of an uron accelerator to an epoxy–DDA formulation reduces the T_g . The authors explained this phenomena by the formation of 1–3 oxazolidin-2-one, which can react further with DGEBA. The initial amine-to-epoxy ratio value influence on the cured resin T_g was also analyzed.^{6,8} Seeing the complexity of the reactions involved in DDA–epoxy systems, only empirically optimized formulations are generally used, and it seems very important to improve the knowledge of curing mechanisms for such a widely used system.

The aim of the present work is to clarify first the influence of the DDA–epoxy function stoe-

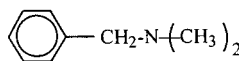
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**LY 556 (DGEBA $n=0.15$)****DYHARD (DDA) 100 S or 100 SF****DYHARD substituted ureas**

$R_1 = H$; $R_2 = H$: Fenuron

$R_1 = H$; $R_2 = Cl$: Monuron

$R_1 = Cl$; $R_2 = Cl$: Diuron

**BDMA/Benzyltrimethylamine****Figure 1** Structure of reactants.

chiometric ratio. Secondly, different urones were introduced, and the influence on kinetics and conversion at gelation and mechanism were studied. The influence of the amount of added urones was also studied and related to the physical properties of the final networks.

This study is a part of a wider program concerning the solventless elaboration of prepreps and composite materials.

EXPERIMENTAL

Materials

The chemical system used was based on a liquid difunctional epoxy diglycidyl ether of bisphenol A (DGEBA), LY 556 (Ciba Geigy) with an equivalent

epoxy of 182 g/eq cured with dicyandiamide (DDA) and accelerated by substituted ureas or a tertiary amine [Benzyltrimethyl amine (BDMA)]. The material structures are shown in Figure 1. DDA from SKW Trotsberg was used in micronized forms with 2 granulometries : DYHARD 100S (98% of particle diameters lower than 10 μm ; called DDA₁₀) and DYHARD 100SF (98% of particle diameters lower than 5.3 μm ; called DDA₅). 1.6 and 4% of SiO₂ were respectively present in the DDA powder to facilitate its processing. This SiO₂ content was subtracted for calculating the molar ratio. The following urones were used : FENURON (*N,N*-dimethyl-*N'*-phenylurea, DYHARD UR300), MONURON (*N,N*-dimethyl-*N'*-(4-chloro)phenylurea, DYHARD UR300) and DIURON (*N,N*-dimethyl-*N'*-(3,4-dichloro)phenylurea, DYHARD UR200). These urones were used

in a micronized form with 98% < 100 μm ; they are commercialized by SKW Trotsberg. BDMA (benzyltrimethylamine) was also used as a catalyst ($M = 135 \text{ g mol}^{-1}$; Fluka).

All reactants were used as received without further purification. The samples used in the present experiments were prepared by mixing the epoxy prepolymer with the desired amount of DDA and accelerator using mechanical stirring and under vacuum; a/e is defined as the molar ratio of DDA to epoxy functions, and the calculations were made assuming that the DDA functionality was 4, even if it was reported that this functionality was not correct.^{3,7,8}

Techniques

Calorimetry

Differential scanning calorimetry (DSC) analysis was recorded with a microcalorimeter, METTLER TA-3000. DSC measurements were performed under argon atmosphere with a heating rate of $q = 10 \text{ K/min}$ during the first scan and $q = 7.5 \text{ K/min}$ during the second scan. The degree of cure was determined with the following equations: $X_{\text{DSC}} = 1 - \Delta H_{(t)}/\Delta H_{(o)}$ with $\Delta H_{(t)}$; residual reaction enthalpy at time t and $\Delta H_{(o)}$; and total reaction enthalpy at $t = 0$. The samples were first cured in an oven maintained at isothermal temperature (80°C), then cooled, and finally tested by DSC. Certain information can be obtained: glass transition temperature (T_g), initial exothermal temperature (T_i), maximum exothermal temperature (T_p), final exothermal temperature (T_f), and residual reaction enthalpy (ΔH).

Size Exclusion Chromatography

Size exclusion chromatography (SEC) was carried out using a Waters chromatograph equipped with a 510 pump, a U6K injector, a 486UV detector set at $\lambda = 254 \text{ nm}$, and a RI410 differential refractometer. Tetrahydrofuran (THF) was used as an eluent solvent, and an separation was carried out over 2 microstyrigel columns (500 and 100 \AA) with an elution rate of 1 mL/min . The samples were first cured at isothermal temperature (80°C) in an oil bath, then cooled, and, finally, solutions at 1% THF by weight were prepared, filtered using a $0.45 \mu\text{m}$ filter, and tested. Assuming the equireactivity of epoxy groups,¹⁴ we can determine $X_{\text{SEC}} = 1 - (S_{(t)}/S_{(o)})^{1/2}$ where $S_{(t)}/S_{(o)}$ is the ratio of the actual surface of DGEBA peak ($n = 0$) to the initial one.

Infrared Spectroscopy

Fourier transform infrared (FTIR) spectroscopy was performed using a Nicolet Magna-IR 550 spectrometer. An Ever-Glo™ source was used, along with a KBr beamsplitter and a DTGS-KBr detector. The mid-infrared (MIR) spectra were recorded in the $400\text{--}4000 \text{ cm}^{-1}$ range. The windows for the transmission cell were KBr disks. No spacer was used because of the need of a very small sample path length. The near-infrared (NIR) spectra were recorded in the $4000\text{--}7000 \text{ cm}^{-1}$ range. The windows for the transmission cell were glass disks using a 0.04 mm lead spacer. Isothermal experiments were carried out in a heated cell (Power Process Controls 355-A) set at $80 \pm 1^\circ\text{C}$. Each spectra represents the sum of 32 individual scans with 4 cm^{-1} resolution. The epoxy combination band at 4530 cm^{-1} is used with an internal standard (phenyl combination band at 4065 cm^{-1}).¹⁵ Epoxy conversion is given by $X_{\text{FTIR}} = 1 - A_{(t)}/A_{(o)}$, where $A_{(t)}/A_{(o)}$ is the ratio of the normalised area of the peak at time t to the initial one and $A_{(t)}$ is the ratio of the area of the epoxy peak to the phenyl vibration band peak.

RESULTS AND DISCUSSION

DSC Measurements and Epoxy Conversion Determination

Information obtained by DSC measurements can be related to the network structure¹⁵ or to the reaction conversion.¹⁶ The reaction enthalpy ΔH corresponds to the overall reactions, including those concerning the epoxy function consumption and secondary reactions. In opposition, in the case of the DGEBA–Jeffamine system, it was shown that ΔH provides for the true epoxy conversion due to the presence of a unique polycondensation mechanism.¹² T_i , T_p , and T_f values give information for the choice of processing parameters, especially curing temperature.

As reported previously,¹⁵ with the same reactive system, the FTMIR analysis was a good tool for epoxy conversion measurements and which agree well with chemical titration and size exclusion chromatography. Experiments were made at 80°C using a DDA–DGEBA system ($a/e = 0.6$) accelerated by DIURON (3% by wt).

Results from DSC, corresponding to specimens cured in DSC cells in an oven (*ex-situ* experiments) were compared to those obtained in a heating cell using FTNIR analysis (Fig. 2). (These

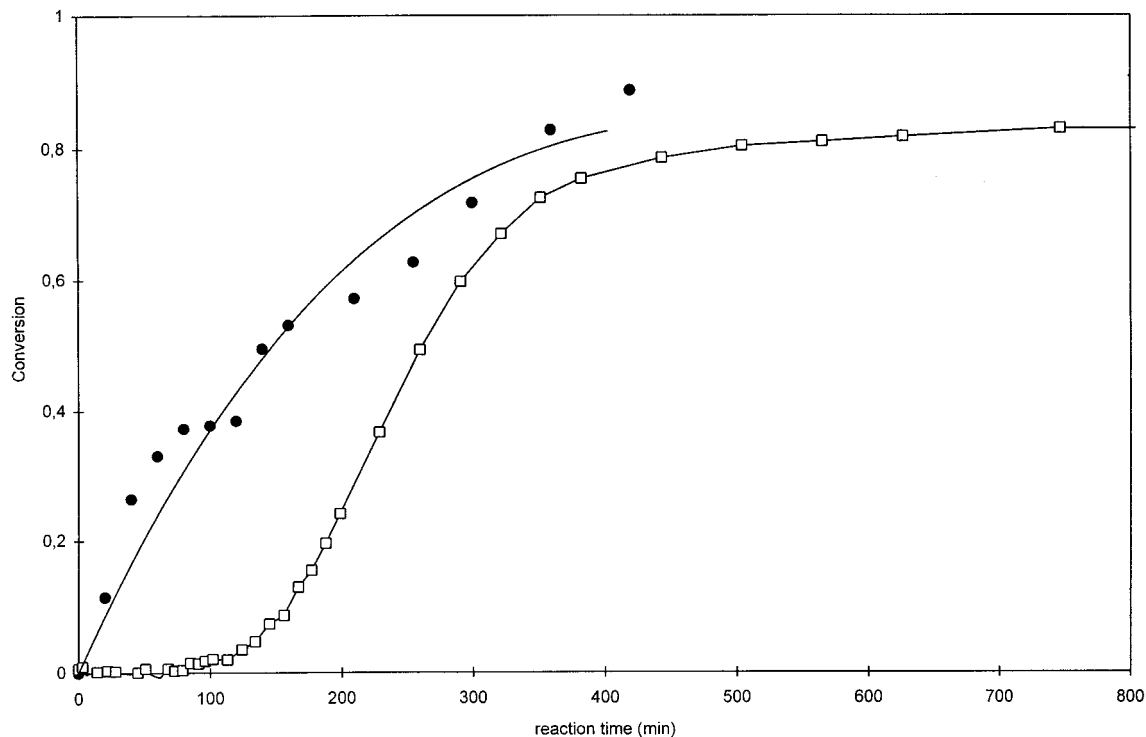


Figure 2 Conversion versus reaction time at 80°C for the system DGEBA-DDA ($a/e = 0.6$) using 3% by weight of DIURON. Conversions measured by FTNIR (□) and DSC (●).

experiments were repeated 3 times, and equivalent results were obtained for each technique).

Different developments were obtained. A 100 min latency was observed with FTNIR analysis, while no latency appeared using DSC. In addition, T_g values, corresponding to specimens cured during the latency period observed by FTNIR, remained constant (Fig. 3).

It is clear, from previous observations in the literature,^{18,19} that the latency observed is due to the dissociation of URONS into isocyanate and dimethylamine.⁸ Sometimes, the difference obtained using the DSC and FTNIR analysis was attributed to a catalytic effect of water moisture or aluminium pans. In order to examine such hypotheses, experiments were made using the DSC oven to cure the system (*in-situ* experiments). As seen in Figure 4, the latency is now recovered showing that the hypotheses mentioned above are not correct.

It was then concluded that the recorded ΔH does not correspond only to epoxy consumption and that other reactions (dissociation of urons, formation of intermediate species) may be present.

In addition, a part of ΔH might not be measured because of the difference between the isothermal curing temperature and the initial exothermal temperature ($T_i = 130^\circ\text{C}$), but this assumption is probably not the only reason for the large difference obtained.

It should be noticed that the degree of curing (determined by DSC) is higher than the epoxy conversion (determined by DSC), and is higher than the epoxy conversion (determined by FTIR), as already mentioned.⁷ Thus, for partially cured samples, the residual reaction enthalpy depends not only on epoxy conversion but also on the curing temperature, indicating a competition between the different reaction paths.

In conclusion, if information about the quantitative conversion given by ΔH is not correct, especially for the commonly used *ex-situ* DSC monitoring, that given by T_g , corresponding to the network structure, seem to be pertinent and can be discussed further.

Influence of DDA Content

Due to the complex reaction mechanisms,¹⁻⁴ the influence of the DDA-to-epoxy molar ratio has

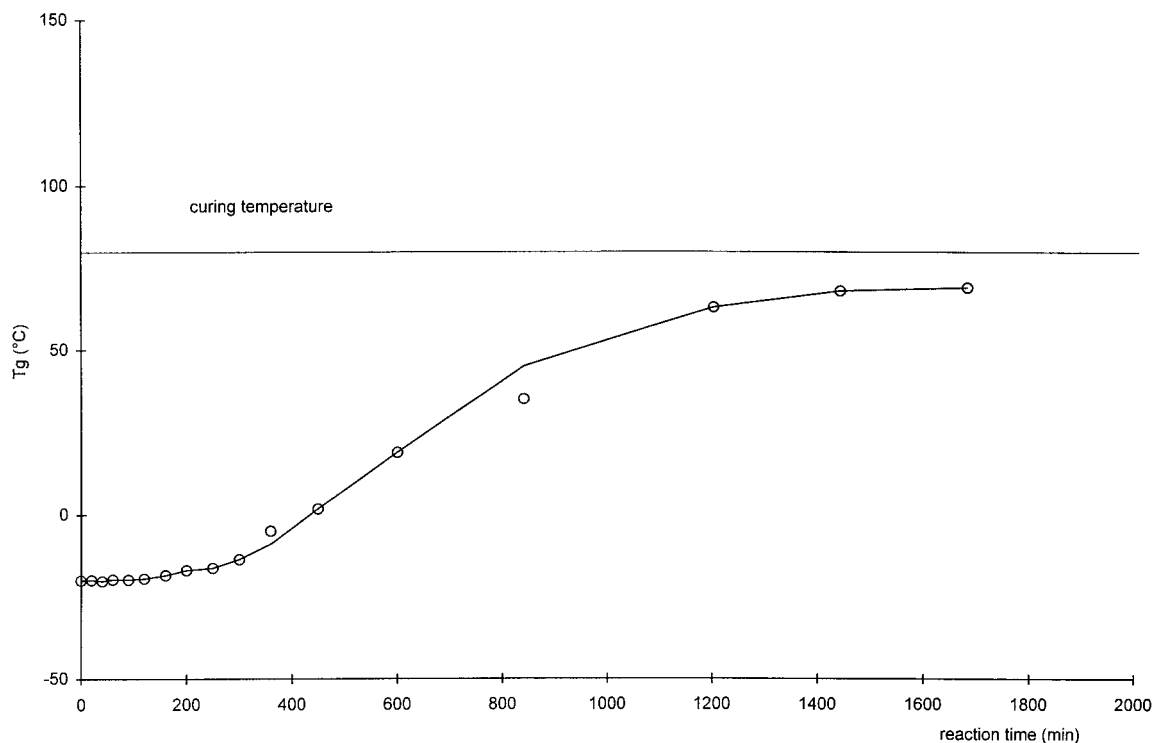
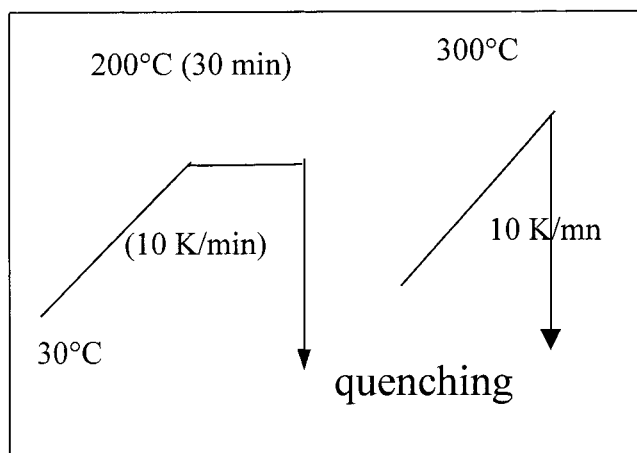


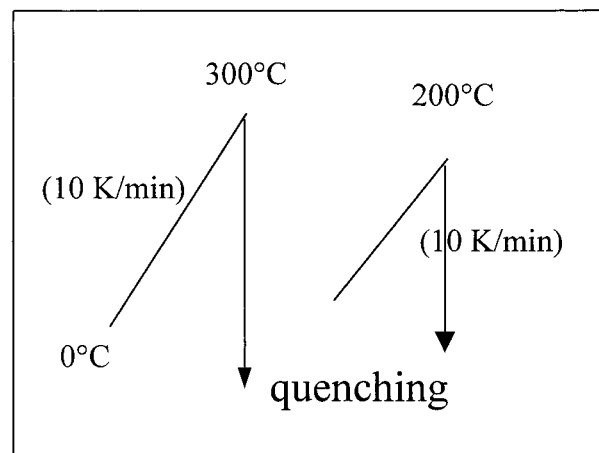
Figure 3 T_g versus reaction time during the same DSC measurements plotted in Figure 2.

been largely studied. Some recent investigations⁸ showed that a maximum T_g value was obtained for a nonaccelerated system for an amine-to-epoxy ratio equal to 0.52. This result is different from the value of $a/e = 1$ found generally with other classical amines⁶ as diaminodiphenylsulfone (DDS) or diaminodiphenylmethane

(DDM). For BDMA accelerated DDA-DGEBA systems, the value 0.6 was found.⁶ It is, therefore, necessary to clarify this aspect, and we have studied the influence of a/e on the T_g values. For this purpose, we used 2 curing cycles described in the literature: cycle 1⁶ and cycle 2,⁸ which are summarized below (Scheme 1).



Cycle 1



Cycle 2

Scheme 1

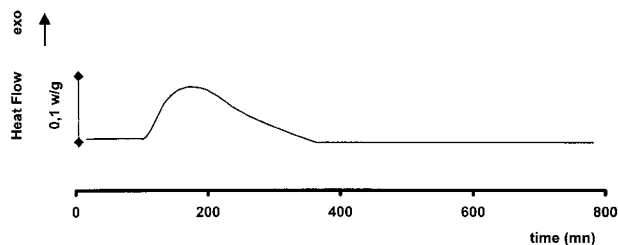


Figure 4 *In-situ* DSC measurements of the mixture containing DGEBA-*DDA* ($a/e = 0.6$) and DIURON (3% by weight); isotherm at 80°C.

The influence of the stoichiometric ratio a/e for a nonaccelerated system is plotted on Figure 5, a quasi-constant T_g value was obtained for $0.5 \leq a/e \leq 0.7$ for the 2 curing schedules, and a slow decrease for higher a/e . These results concerning the influence of the stoichiometric ratio are in agreement with those of Günther and Hammer,⁸ even if the maximum of a/e was not so well defined.

Günther and Hammer⁸ proposed an explanation of the low a/e value, leading to a T_g maximum. This explanation is based on FTMIR mon-

itoring of the epoxy (915 cm^{-1}), cyano (2180 cm^{-1}), imino (1685 cm^{-1}), and cyanamino (1560 cm^{-1}) bands using the phenyl band (830 cm^{-1}) as an internal standard. They concluded that the stoichiometric reaction involves 7 epoxy units per mol *DDA*, explaining the low a/e value. Moreover, it was shown recently that the band attributed to epoxy at 915 cm^{-1} is not really representative of this function and that its use for the establishment of a reaction mechanism can be contested.¹⁷ In addition, due to the low soluble *DDA* concentration at the initial reaction stage, an epoxy homopolymerization cannot be excluded. These facts can explain the small discrepancy between our results and those of Günther and Hammer.⁸ An attempt was made to explain these mechanisms by FTIR spectrometric analysis, as Mijovic et al.²¹ did, but neither with NIR or MIR, NH and NH_2 bands were found to be sufficiently clear to show a real evolution.

Influence of DDA Particle Size

A good dispersion of solid *DDA* in epoxy prepolymer is necessary in order to obtain reproducible

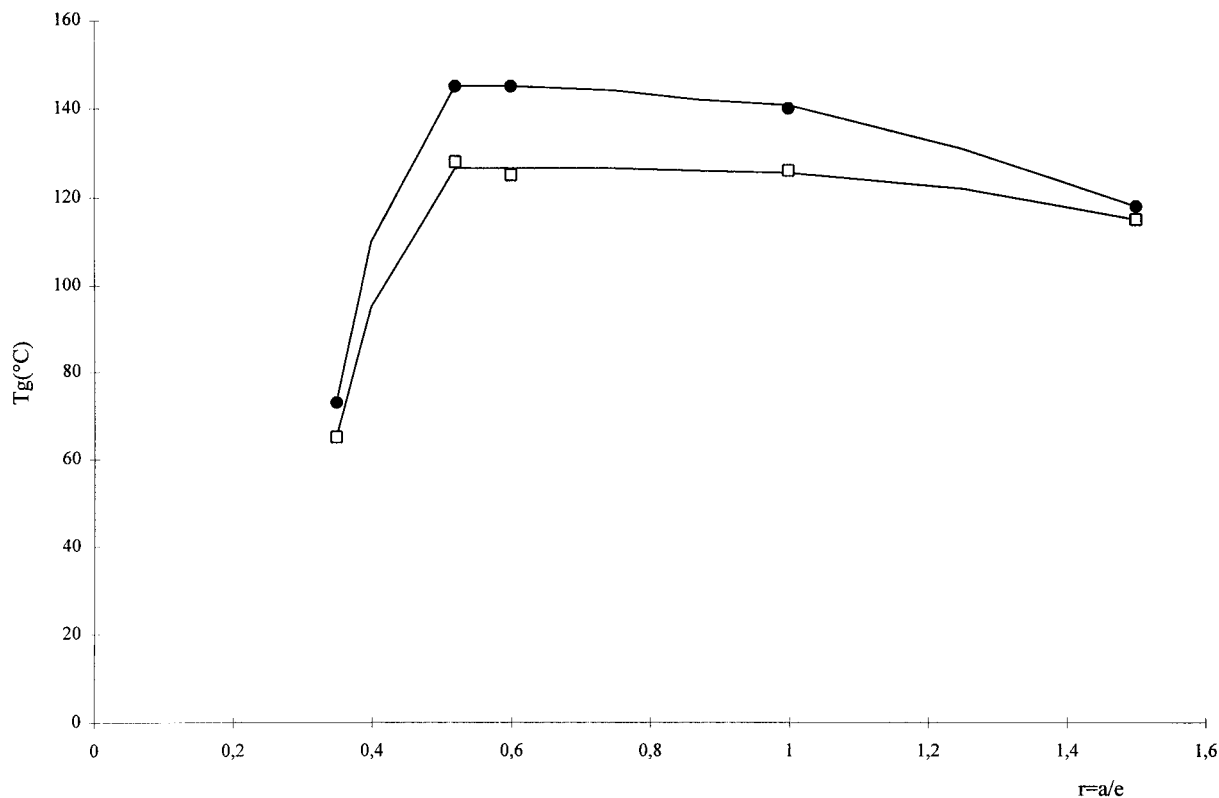


Figure 5 T_g of nonaccelerated systems using the following 2 curing schedules : cycle 1⁶ (□) and cycle 2⁸ (●) and a different amine-to-epoxy molar ratio.

Table I Influence of DDA Particle Size: T_g for Cycle 1⁶ and Cycle 2⁸

| Formulations DDA | Cycle | DGEBA-DDA (0.52) | | DGEBA-DDA (0.6) ^a | |
|---------------------|-------|------------------|-------------------|------------------------------|-------------------|
| | | DDA ₅ | DDA ₁₀ | DDA ₅ | DDA ₁₀ |
| T_g (°C) | 1 | 129 | 138 | 114 | 119 |
| T_g (°C) | 2 | 145 | 145 | 110 | 115 |

^aWith accelerator (FENURON 3% by weight)

reaction kinetics and final conversion. Solubility and diffusion of reactive species can be influenced by the DDA granulometry, which can thus modify the latency period and the reactivity.

For the mixture DDA₁₀-DGEBA, where $a/e = 0.52$, without accelerator, T_g values determined with cycle 1 are lower than those obtained with DDA₅, and no differences were found with cycle 2 (Table I).

A similar experience was carried out with the addition of 3% by wt of FENURON to DGEBA-
DDA mixtures ($a/e = 0.6$) (Table I). In this case,

the T_g values with DDA₁₀ are a slightly lower than those obtained with DDA₅.

In order to check if DDA particle size really affects the reactivity, we followed the epoxy conversion by SEC during the isothermal reaction at 80°C (Fig. 6) using DDA₅ and DDA₁₀.

The results indicate that there was no noticeable influence of DDA particle size on the kinetics at low temperature and that the etherification mechanism, which can explain the T_g difference, occurs only at high temperature. So DDA granulometry seems not to be a dominant parameter,

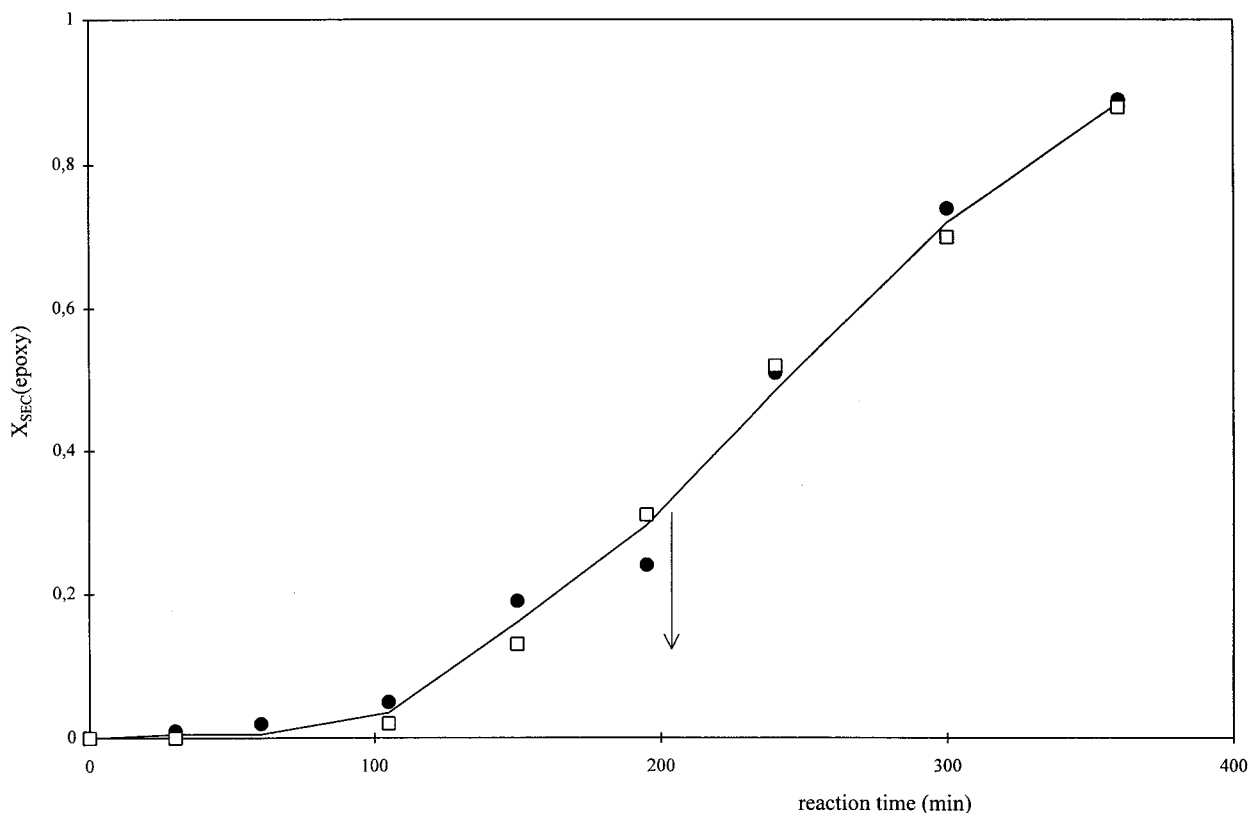


Figure 6 Epoxy conversion measured by SEC versus reaction time at 80°C for the system DGEBA-
DDA ($a/e = 0.6$) system and DIURON (3% by weight) for the following 2 DDA particle sizes : (●) DDA₅ and (□) DDA₁₀. The arrow indicates gelation.

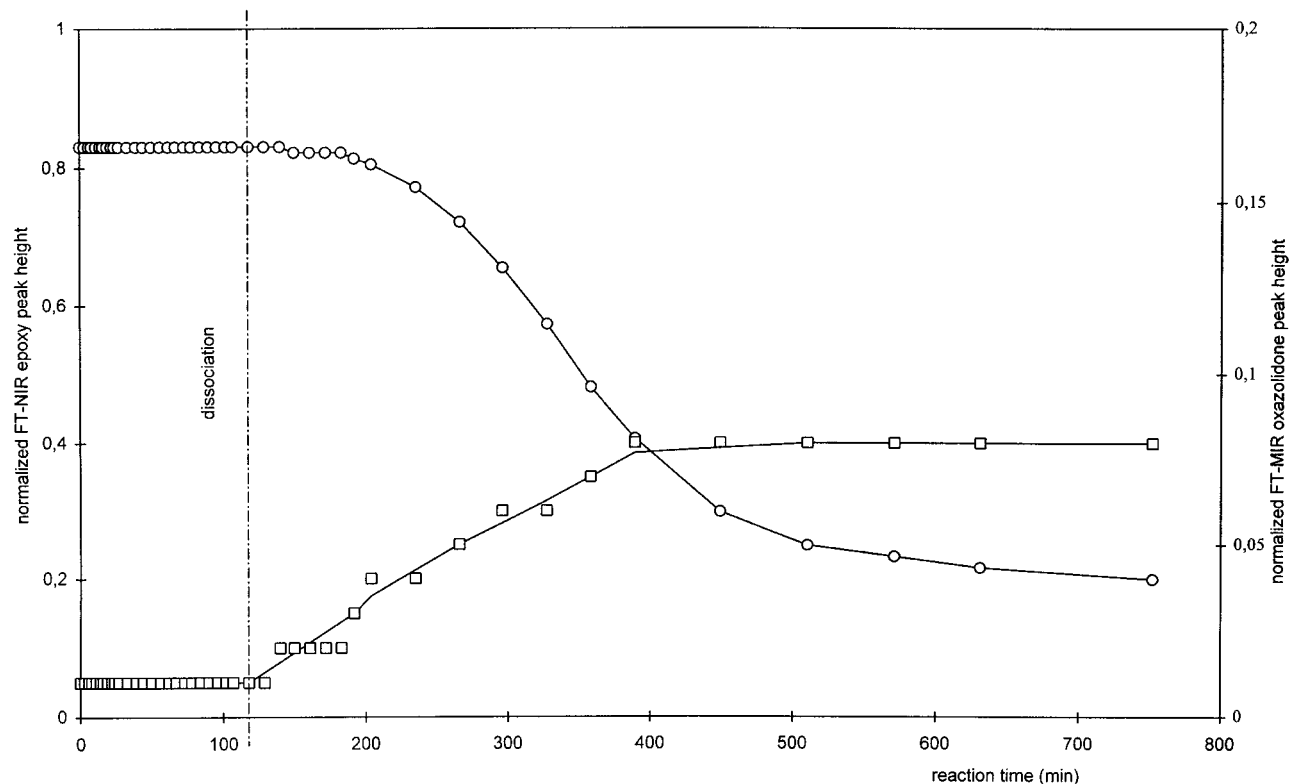


Figure 7 Normalized oxazolidone peak measured by FT-MIR (□) and normalized epoxy peak height measured by FT-NIR (○) versus reaction time at 80°C for DGEBA–DDA ($a/e = 0.6$) and DIURON (3% by wt).

and DDA₁₀ should be preferred industrially, since it is easier to manipulate (no agglomeration), and should be used in the following studies.

It has to be noticed that the introduction of FENURON decreases the T_g of networks, and this fact will be discussed in the next part.

Influence of Urone Nature and Content

The introduction of urones and their dissociation leads to the formation, first of dimethylamine, and then to tertiary amine, that catalyzes the epoxy–DDA reaction.^{11–13} As was shown previously, a latency period is obtained, and it is interesting to study such a reaction mechanism.

IR spectra in the 1800–750 cm^{-1} range are recorded for the mixture containing DGEBA–DDA ($a/e = 0.6$) and DIURON (3% by wt) cured *in-situ* at 80°C at different reaction times. The relevant feature is the increase in the absorption of the oxazolidone peak^{8,11,13} at 1760 cm^{-1} that is correlated to tertiary amine formation when increasing the curing time. As was shown in a recent publication,¹⁷ a parallel NIR spectroscopy

study was carried out to quantify the epoxy disappearance because of the invalidity of 915 cm^{-1} epoxy band.

A clear dependence between both evolutions was observed (Fig. 7). These results confirm that the reaction starts with the DIURON dissociation.

The issued dimethylamine reacts with an epoxy, leading to a tertiary amine that catalyzes the DDA–epoxy reaction, while the isocyanate reaction with epoxy leads to an oxazolidone function.

These results agree with the mechanisms suggested by G uthner and Hammer.⁸

This mechanism infers the following important remarks.

1. Since a part of the epoxy functions reacts with the DIURON dissociation products, the a/e ratio changes during reaction
2. The DIURON dissociation produces a reaction with the epoxy functions and leads to nonreactive functions. The DIURON, acting as a chain termination agent, leads to dangling chains

Table II T_g Versus DIURON Weight Percentage for Accelerated DGEBA-DDA (0.6) Mixtures

| Weight (%) | T_g (°C) ^a |
|------------|-------------------------|
| 0 | 133 |
| 2 | 125 |
| 3 | 123 |
| 4 | 113 |

^aCycle 1.⁶

3. DIURON is not a catalyst but an accelerator.

From these remarks, it is clear that the addition of DIURON changes the network structure and then the T_g . This was confirmed in the data reported in Table II, where an increase in DIURON concentration resulted in a decrease of the T_g of the cured resin.

In Figure 8, we study the influence of the amount of DIURON on the epoxy conversion kinetic at 80°C using SEC analysis. As expected,

increasing the quantity of accelerator reduces the latent period and increases the reaction rate. The epoxy conversion at gelation, determined using insoluble fraction detection, decreases if the amount of DIURON increases, confirming the fact that the products resulting from the dissociation are involved in the network structure.

Effect of the Accelerator Type

In order to study the influence of the accelerator nature, we performed 2 experiments, with DIURON (3% by wt) and BDMA with the same molar ratio (5.6%). The epoxy conversion versus time at 80°C is presented in Figure 9. The first difference is the strong accelerating effect due to the tertiary amine BDMA compared with the DIURON. In the case of DIURON, it has to be dissociated before, and the tertiary amine has to be formed when it was present at the initial time with BDMA. The second difference is the epoxy conversion at gelation, which is close to 0.74 (as a pure polycondensation reaction); in the case of the BDMA-catalyzed system, is ≈ 0.3 for the DIU-

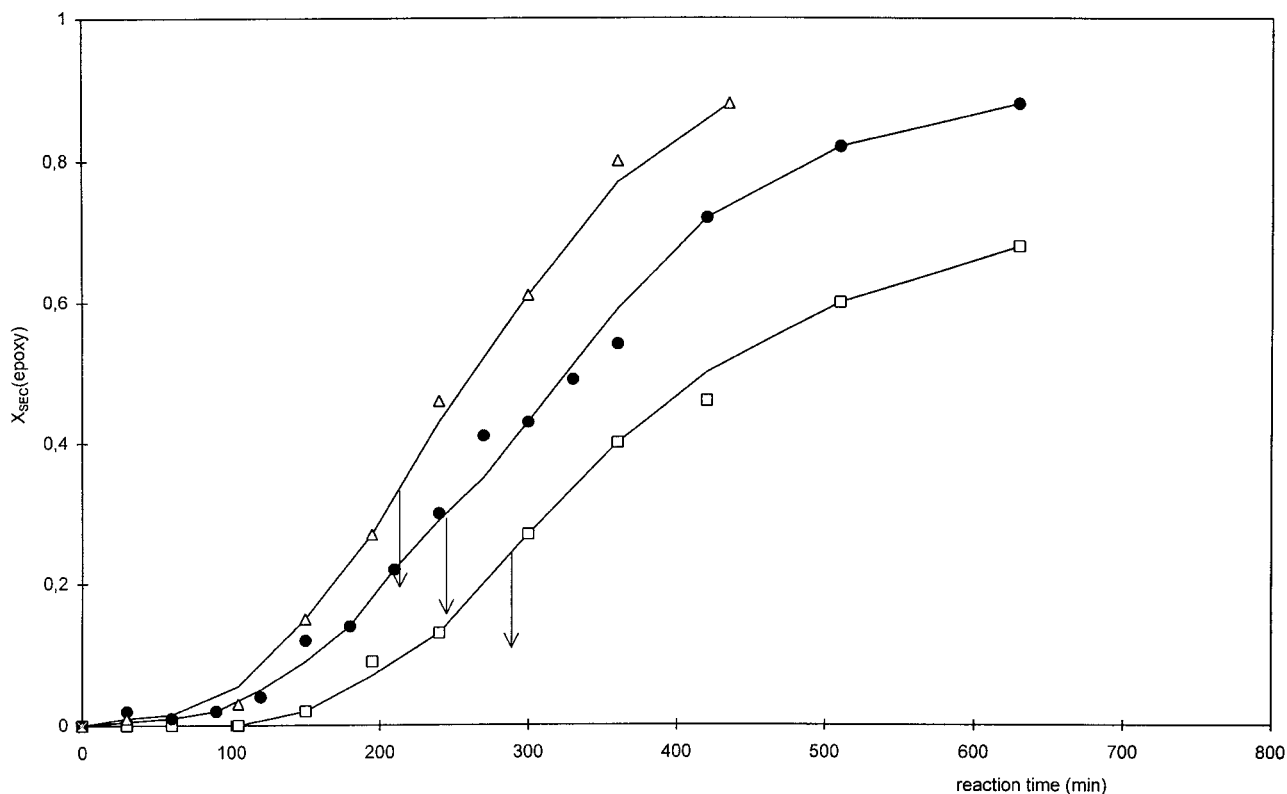


Figure 8 Effect of DIURON concentration on epoxy conversion measured by SEC for DGEBA-DDA ($a/e = 0.6$) reaction at 80°C. The percentage of DIURON by weight : (□) 2%; (●) 3%; (Δ) 4%. Arrows indicate gelation.

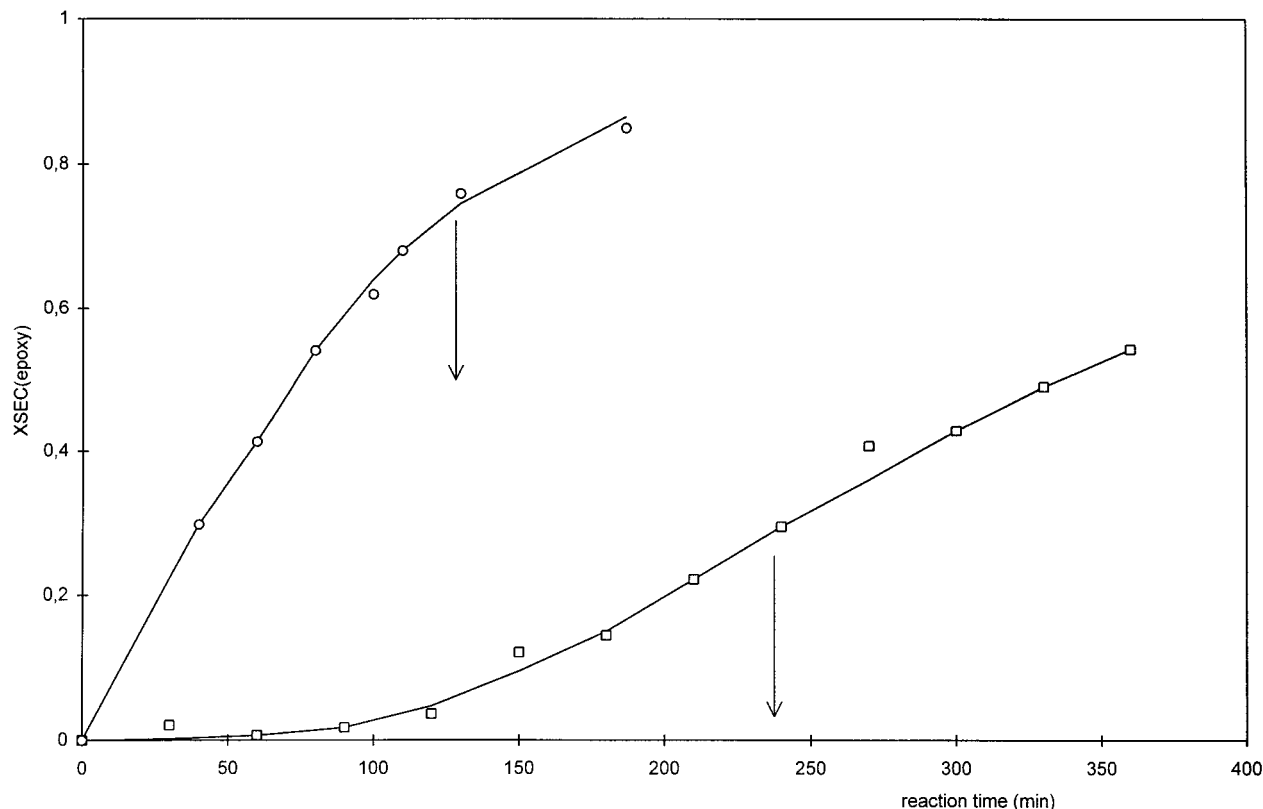


Figure 9 Epoxy conversion measured by SEC for DGEBA-DDA ($a/e = 0.6$) reaction at 80°C using 3% by weight DIURON (□) or 1% by weight BDMA (●). Arrows indicate gelation.

RON-accelerated system. This means that a very little propagation, or etherification occurs in the BDMA catalyzed system at this temperature. The chemical nature of the urones can also influence the reactivity, and we studied the influence of DIURON and FENURON using the same molar ratio (5.6%). The stoichiometric ration a/e was kept constant and equal to 0.6.

The characteristic temperatures T_i , T_p , and T_f (Table III) and the kinetics (Fig. 10) are not affected by the change of urone nature according to a previous article.²² However, some significant variations about gel conversion are noted. Using DIURON leads to a higher gel conversion than FENURON, and FENURON acts like a smaller amount of DIURON. With DIURON, the network is characterized by a lower T_g (116°C) than the one obtained with FENURON (119°C). This phenomenon can be explained by the higher reactivity of the isocyanate produced from the diuron dissociation due to the presence of 2 chlorine atoms (Fig. 1).²²

CONCLUSION

An investigation of URON-accelerated DGEBA-DDA systems has been carried out. It was found that calorimetric measurements are not convenient for reaction rate monitoring and that SEC or IR spectroscopies are more specific and accurate. The very complex reaction mechanism of DDA makes the study of the influence of DDA

Table III Exothermal Temperatures for Accelerated DGEBA-DDA ($a/e = 0.6$) with FENURON, MONURON, and DIURON^a

| Accelerators | [Urone]/[Epoxy] = 0.056 | | |
|--------------|-------------------------|---------|--------|
| | FENURON | MONURON | DIURON |
| T_i (°C) | 130 | 131 | 131 |
| T_p (°C) | 156 | 156 | 157 |
| T_f (°C) | 198 | 196 | 192 |

^aDSC Experiments at 10 K/min.

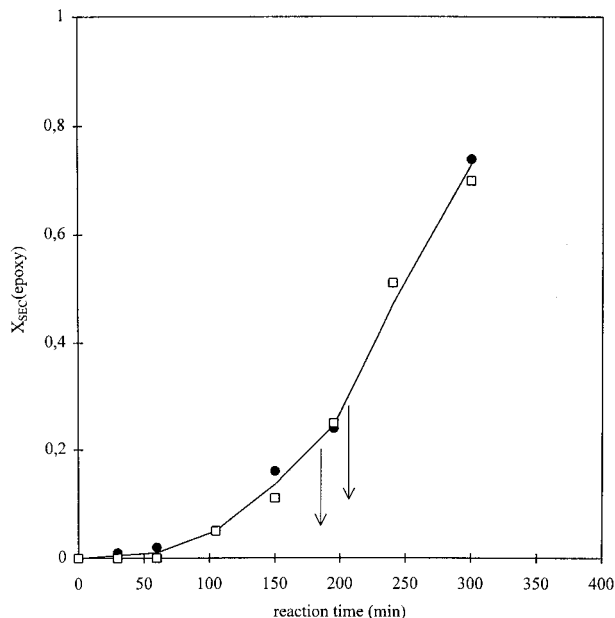


Figure 10 Epoxy conversion measured by SEC versus reaction time for DGEBA–DDA reaction at 80°C $a/e = 0.6$ accelerated by 4.26% by weight DIURON (□) or 3% by weight FENURON (●). Arrows indicate gelation.

amount on T_g values a very important parameter. The highest T_g values were obtained on a plateau zone for an amine-to-epoxy ratio between 0.5 and 0.74. The DDA particle size seems not to be a predominant parameter on the reaction rates at 80°C.

An induction period was shown during the isothermal cure at 80°C, corresponding to the dissociation of DIURON and the appearance of oxazolidone rings characterized by IR spectroscopy.

During isothermal cure at 80°C, if the initial amount of DIURON increases, it induces a decrease in T_g and gel conversion, showing that URON is more of an accelerator than a catalyst. The comparison of FENURON and DIURON, at the same molar ratio, led us to the conclusion that there was no effect on the reaction rate but only a slight difference in gel conversion.

The mechanical properties of the final networks and the toughening effect of siloxane particles will be the subject of a further article.

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