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Tuning morphologies of thermoset / thermoplastic blends Part 1: Kinetic modelling of epoxy-amine reactions using amine mixtures

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Abstract: Different epoxy amine networks based on a mixture of diamine hardeners have been studied and their kinetic behaviour was modelled in order to understand the global and particular behaviour of each diamine in such blends. 4,4'-Diaminodiphenylsulfone (DDS) and 4,4'-methylenebis-(3-chloro-2,6-diethylaniline) (MCDEA) were used for this study by varying the DDS molar ratio from 0% to 50%. The determined kinetic model allowed us to calculate the composition for each diamine of the reactive epoxy-amine system in the whole range of epoxy conversions. Then the influence of 10% thermoplastic additive was checked and it was found to be negligible in the kinetic behaviour.

Introduction

High T_g epoxy thermosets are widely used in industry when good mechanical and thermal properties are required. However, the high level of crosslinking in epoxy networks lead to brittle materials. Since the early 1980s the incorporation of an initially miscible thermoplastic (TP), which phase separates during the epoxy/hardener reaction, has often been used as a way to improve the toughness of epoxy networks [1, 2]. This extra component, called the modifier or the toughener, is initially miscible with the resin and curing agent. Reaction-induced phase separation is caused by the reduction of solubility due to the increasing average molar mass of the polymer. Phase separation starts *in situ* at the "cloud-point" conversion (x_{cp}) and when the matrix gels, this primary separation is practically finished [3, 4]. After gelation, a secondary phase separation may continue inside the dispersed phase. Predominant parameters that affect the final morphology include the content of modifier, the reactivity of the hardeners, the cure temperature and the "cloud-point" viscosity (η_{cp}). Several authors have investigated the influence of cure schedules on the resulting morphology. Most of the time studies concern the cure temperature [5-12]. Some work has been reported on the effect of varying heating rates [13, 14]. Fang et *al* [14] elaborated "sandwich" structures due to the different heating rates between core and layers. In order to control the morphology of the separated phase, the potentiality of using a mixture of two hardeners has been seldom mentioned or used in previous studies [15, 16]. Although industrial thermosetting epoxy/amine formulations are often composed of mixtures of epoxy and amine molecules, literature reveals very little experimental work and modelling of the reaction of complex epoxi(es)/amine(s) formulations, e.g. one or several epoxy resins with a mixture of different hardeners (e.g. several amines). There exists some related studies concerning mixtures of amines of different functionalities (mono + diamines [17, 18] or di + tri amines [16], mixtures of diamines having different chain lengths leading to “bi modal epoxy networks” [19], mixtures of two epoxy oligomers having different functionalities crosslinked with one diamine [20]). Indeed by using such systems in thermoset / thermoplastic (TS/TP) blends, both the reactivity and the degree of miscibility of the blend might be adjusted by changing the proportion of each hardener. In the case of amine hardeners, the choice of two diamines, one inducing phase separation and the other one inducing miscibility of the TP, can reveal a good way to tune the size of the TP domains.

However the reaction polymerization modelling of these systems appears to be complex [21] due to the difference in reactivity of each amine [17].

Traditionally, thermoset chemistry specialists tend to characterize kinetics from isothermal experiments using chemical group specific detection techniques [22, 25], their main objective being to establish a detailed reaction mechanism. Nevertheless, in order to estimate with a good accuracy the kinetic parameters of this model, it is often more interesting to perform a kinetic study using calorimetry experiments [24-26], the simplest and widely used thermal method being Differential Scanning Calorimetry (DSC). Nevertheless, the limitation of such thermal methods is that they only give average information. In the case of a complicated reaction pathway, they do not provide sufficient information to understand the chemical pathway.

Numerous studies exist on kinetic models for epoxy-amine resins [27]. The mechanistic models [15, 28], describing the mechanism of each elementary reaction (taking into account substitution effect for primary and secondary amines) are complicated and need sophisticated calculation methods in order to identify an important number of unknown parameters (often with a bad accuracy and more or less justified hypothesis). On the contrary, the phenomenologic models, even based on non justified approximations (as equireactivity of primary and secondary amines), often allows a correct modeling of experimental data.

The aim of the present work is to investigate the cure behaviour of amine mixtures (DDS and MCDEA in different proportions) crosslinked with one epoxy oligomer (DGEBA). The cure kinetics of the epoxy resin will be independently analyzed with the two hardeners. Then, by using the obtained kinetic parameters, the kinetic behaviour of the epoxy resin mixed with various amounts of the two hardeners will be simulated and compared to experimental results. Finally we will explain how this kinetic model can be used to calculate up to the gel point the composition in each amine of the reactive system containing a small % of thermoplastic modifier, namely polyvinyl methylether. The results will be helpful in order to understand the various morphologies obtained as a function of the hardeners ratio initially present in the resin and as a function of the instantaneous concentration of both unreacted amines during phase separation. The results concerning phase separation and morphologies of TS/TP blends are presented in Part 2 of the study.

Results and Discussion

Equations and mechanistic model

The problem of choosing the appropriate kinetic functions often leads authors to oppose two different approaches: model fitting and isoconversional analysis [29].

The model fitting technique is the most widely spread approach [30]. It consists in using empirical kinetic models and fitting them to experimental data. The problem is that usually quite different kinetic functions fit experimental data equally well (from a statistical point of view), whereas the numerical values of the corresponding Arrhenius parameters differ [31].

Therefore, it is necessary to have information a priori about reaction mechanism in order to choose a kinetic function with a physical meaning. This is the case when a (even simplified) kinetic scheme has already been established by other experimental techniques and non isothermal DSC is used as a complementary tool, as it is the case in this study.

Since the purpose of the present work is only to predict the evolution of the conversion during the cure processing, especially at phase separation (in the presence of a modifier) and up to the gel point, a simple model, derived from a mechanistic model, but based on several simplifications will be considered to model the reaction kinetics:

- the substitution effect between primary and secondary amines is neglected
- etherification reactions are neglected
- a complex formation is not took into account [17, 32]

As usual in modeling, the simplest model is first used: if such simplifications do not allow to correctly model experimental data, more sophisticated kinetic models can be proposed.

The kinetic scheme of the reaction of a diepoxy with a diamine can be written as follows:

$$\left.\begin{array}{ll} \text{Non catalytic behavior} & \left\{ \begin{array}{l} E + A_1 \xrightarrow{k_1} E - A_1 \\[1em] E + A_2 \xrightarrow{k_2} E - A_2 \end{array} \right. \\[3em] \text{Autocatalytic behavior} & \left\{ \begin{array}{l} E + A_1 + OH \xrightarrow{k'_1} E - A_1 + OH \\[1em] E + A_2 + OH \xrightarrow{k'_2} E - A_2 + OH \end{array} \right. \end{array}\right\}$$

where E represents an epoxide function, A_1 represents a N-H of the more reactive amine DDS, A_2 represents a N-H of the less reactive amine MCDEA and OH represent a hydroxyl group. k_i, $k_i^{'}$ represents the arrhenian kinetic constants of each described reaction.

Because the reactivity of the primary amine and the secondary amine are supposed to be equal, this kinetic model can be written as follows.
Consumption of epoxide functions:

$$-\frac{d[E]}{dt}=(k_1+k_1^{'}[OH])[A_1].[E]+(k_2+k_2^{'}[OH])[A_2].[E] \qquad \textbf{(1)}$$

Mass balance:

$$\begin{cases} [A_1]+[A_2]=[E]\Rightarrow[A_2]=[E]-[A_1] & \textbf{(2)} \\ [OH]=[E_0]-[E] & \textbf{(3)} \end{cases}$$

Reporting eqt. 2 and eqt. 3 in eqt. 1 gives:

$$-\frac{d[E]}{dt}=(k_1+k_1^{'}[OH]-k_2-k_2^{'}[OH])[A_1].[E]+(k_2+k_2^{'}[OH])[E]^2 \qquad \textbf{(4)}$$

Consumption of amine functions:

$$-\frac{d[A_1]}{dt}=(k_1+k_1^{'}[OH])[A_1].[E] \qquad \textbf{(5)}$$

$$-\frac{d[A_2]}{dt}=(k_2+k_2^{'}[OH])[A_2].[E] \qquad \textbf{(6)}$$

the extent of conversion *x* of epoxide function can be defined as: [E] = [E_0].(1-x)
so that eqt. 3 can be transformed: [OH] = *x*.[E_0] **(7)**
[E_0] is the initial epoxy function concentration defined as $[E_0]=\lfloor A_{1_0}\rfloor+\lfloor A_{2_0}\rfloor$ with [A_{10}] and [A_{20}] the initial concentrations of DDS et MCDEA functions respectively. We define *r* as the initial molar ratio between the initial molar number of MCDEA and DDS: $r=\frac{\lfloor A_{2_0}\rfloor}{[A_{1_0}]}$ and α_1 as the conversion extent of amine 1 function: $\alpha_1=\frac{\lfloor A_{1_0}\rfloor-[A_1]}{[A_{1_0}]}$.
By introducing *r* and α_1 in the definition of the epoxy concentration, we obtain:

$$[E_0]=[A_{1_0}]+[A_{2_0}]=(1+r).[A_{1_0}]\Rightarrow\alpha_1=1-\frac{1+r}{[E_0]}.[A_1]$$

$$\Rightarrow[A_1]=(1-\alpha_1).\frac{[E_0]}{1+r} \qquad \textbf{(8)}$$

Introducing eqn. 8 and the definitions of the conversion in eqn. 4 and 5 gives:

$$[E_0]\frac{dx}{dt}=\left[(k_1-k_2)+(k_1^{'}-k_2^{'}).[E_0].x\right]\frac{[E_0]^2}{1+r}(1-\alpha_1)(1-x)+(k_2+k_2^{'}.[E_0].x)[E_0]^2(1-x)^2 \qquad \textbf{(9)}$$

$$(k_1+k_1^{'}.[E_0].x)\frac{[E_0]}{1+r}(1-\alpha_1)(1-x)=\frac{[E_0]}{1+r}\frac{d\alpha_1}{dt} \qquad \textbf{(10)}$$

so that final equations can be derived:

$$\begin{cases} \dfrac{dx}{dt} = \left[(k_1 - k_2) + (k_1^{'} - k_2^{'}).\left[E_0\right].x\right]\dfrac{E_0}{1+r}(1-\alpha_1)(1-x) + (k_2 + k_2^{'}.E_0.x)E_0\,(1-x)^2 & \textbf{(11)} \\ \dfrac{d\alpha_1}{dt} = (k_1 + k_1^{'}.\left[E_0\right].x)\left[E_0\right](1-\alpha_1)(1-x) & \textbf{(12)} \end{cases}$$

with: $x = \dfrac{\left[E_0\right] - \left[E\right]}{\left[E_0\right]}$ $\quad r = \dfrac{\left\lfloor A_{2_0} \right\rfloor}{\left[A_{1_0}\right]}$ $\quad \alpha_1 = \dfrac{\left\lfloor A_{1_0} \right\rfloor - \left[A_1\right]}{\left[A_{1_0}\right]}$

(1: DDS; 2: MCDEA)

By integrating this model, one will be able to calculate the instantaneous concentrations [E], [A_1] and [A_2] as a function of time.

In order to solve this equation, one must know:

- the kinetic parameters of the two neat systems DGEBA/DDS (k_1, k'_1) and DGEBA/MCDEA (k_2, k'_2) (obtained from pure amine/DGEBA experiments)
- the initial ratio r.

Practically, the kinetic behavior of these two formulations was measured using DSC experiments. DSC signal *W* obtained for a reactive thermoset sample submitted to a temperature ramp can be divided into two contributions [33]:

$$W = C_P\, q - \Delta_r H \, \frac{dx}{dt} \qquad \textbf{(13)}$$

$$\text{and} \quad T(t) = T_0 + q\, t \qquad \textbf{(14)}$$

In eqn. 13, *q* is the heating rate (K/ min) and C_p is the heat capacity of the sample (J/g/K). This first term $\{Cp.q\}$ corresponds to the baseline in opposition to the heat source term $\left\{-\Delta_r H \dfrac{dx}{dt}\right\}$ due to exothermal reaction, $\Delta_r H$ being the enthalpy of reaction (J/g), x the conversion degree and $\dfrac{dx}{dt}$ the rate of conversion (min^{-1}).

Assuming that $\Delta_r H$ is a constant over all the experimental temperature range [34, 35], it can be measured by integration of the exothermal peak area. Each experiment provides a set of data including time, temperature, rate of conversion and conversion degree.

After obtaining the experimental kinetic data, the Inverse Kinetic Problem [31] consists in finding an appropriate model containing different kinetic parameters and in adjusting these parameters in order to fit the model predictions to the experimental data. As for all inverse parameter estimation methods [36], this implies the minimization of an objective function containing both calculated and measured values of the variable. The simplest objective function is Ordinary Least Squares (OLS) function between model predictions and experimental data:

$$\text{OLS} = \sum \left(x_{theor} - x_{\exp}\right)^2 \qquad \textbf{(15)}$$

Neat systems and determination of kinetic parameters

In the case of a formulation containing only one hardener, the previously described kinetic model simplifies and is written as the simplest Kamal & Sourour model:

$$\frac{dx}{dt} = \left[k_1 + k_1'.[E_0].x\right].[E_0].(1-x)^2 \qquad \textbf{(16)}$$

Different heating rates have been taken: 2°C/min, 3°C/min 5°C/min. The experimental function *x(t)* is determined for the 3 heating rates.

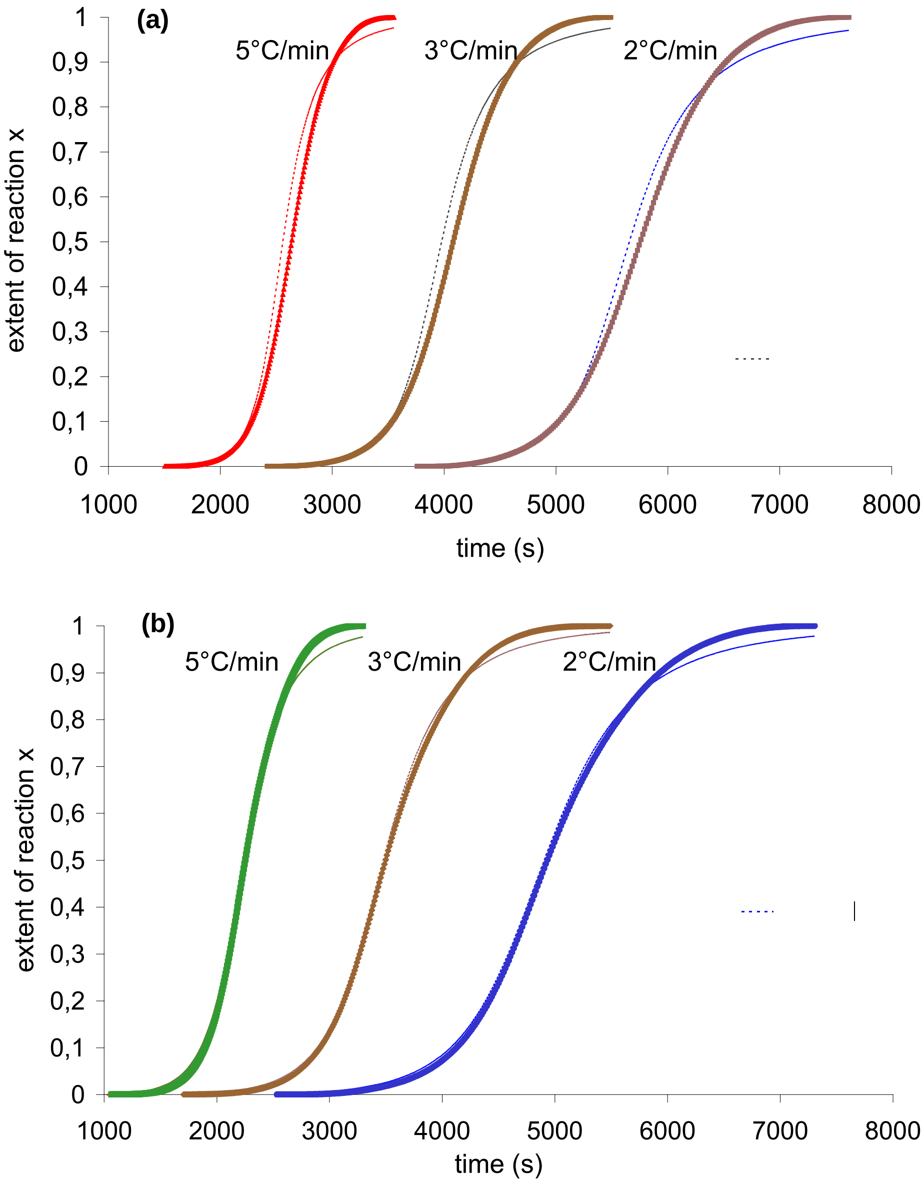


Fig. 1. Epoxy conversion vs reaction time at different heating rates; (- - -) chemical model prediction for the two neat systems: (a) DGEBA-MCDEA; (b) DGEBA-DDS.

Then eqn. 12 is solved with a 4-order Runge Kutta integration technique. The values of time and temperature used during this integration are those previously measured during the DSC experiments. Fitting the theoretical prediction and experimental x(t) values allows the kinetic parameters k_i, k_i', E_i, E_i' to be determined for each amine cured separately (Tab. 1).

This fitting procedure is realized by minimizing the OLS = $\sum\left(x_{theor} - x_{\exp}\right)^2$.

Tab. 1. Kinetic constants for DGEBA cured with DDS or MCDEA.

Formulation	$[E_0]$ (mol/l)	k_i (l/mol/s)	k_i' ($l^2/mol^2/s$)	E_i (kJ/mol)	E_i' (kJ/mol)
100% DDS (i=1)	4,96	$1,94.10^4$	$8,9.10^2$	74	59,5
100% MCDEA (i=2)	4,31	$2,5.10^4$	$1,00.10^3$	82	60,5

Up to elevated conversions, the model appears to fit with a good accuracy the experimental results (Figure 1a and b).

Amine mixtures

These four parameters (from Tab. 2) will be used to predict the conversion of each mixture. As the second part of the study (when a modifier will be added) will concern isothermal cures, several isothermal experiments were performed and compared to simulation (with no more change in the estimated kinetic parameters).

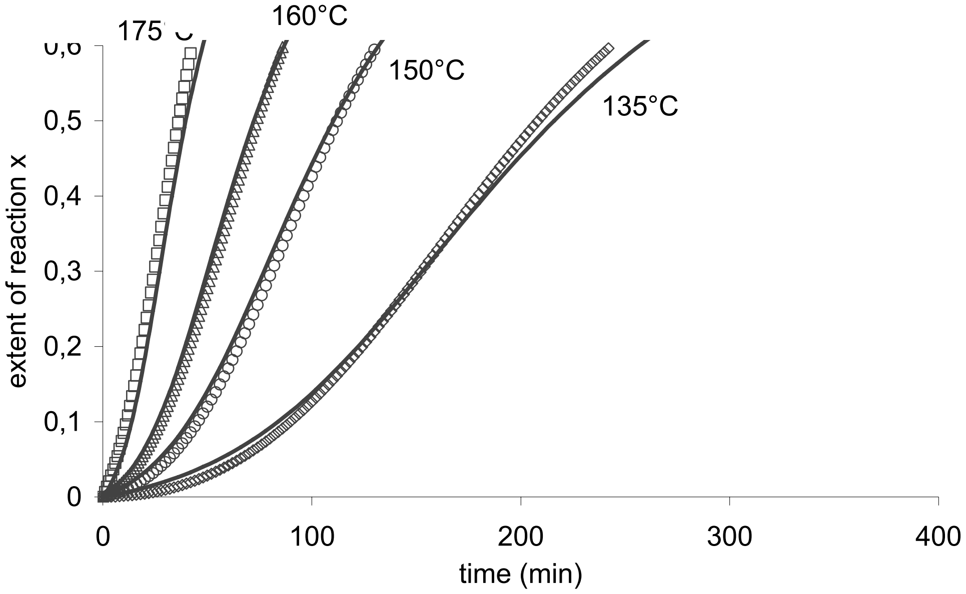


Fig. 2. Epoxy conversion vs reaction time at different cure temperatures for DGEBA/80%MCDEA-20%DDS. Experimental points at : (□) 175°C, (Δ) 160°C, (○) 150°C, (◊) 135°C; Model prediction (—).

According to eqn. 11, it is now possible to model the cure of various mixtures of amines (at different temperatures). Figure 2 and Figure 3 show the result of the modelling for two formulations: DGEBA/80%MCDEA-20%DDS (Fig. 2) and DGEBA/

50%DDS/ 50%MCDEA (Fig. 3). The model is in good agreement until the gel conversion (x_{gel}~0.6) and a difference of no more than 7% is obtained when we compare the model to the experimental curve. Because this model will be used to determine each monomer concentration at the phase separation and because phase separation occurs before gelation, it is not necessary to model the conversions higher than x_{gel} .

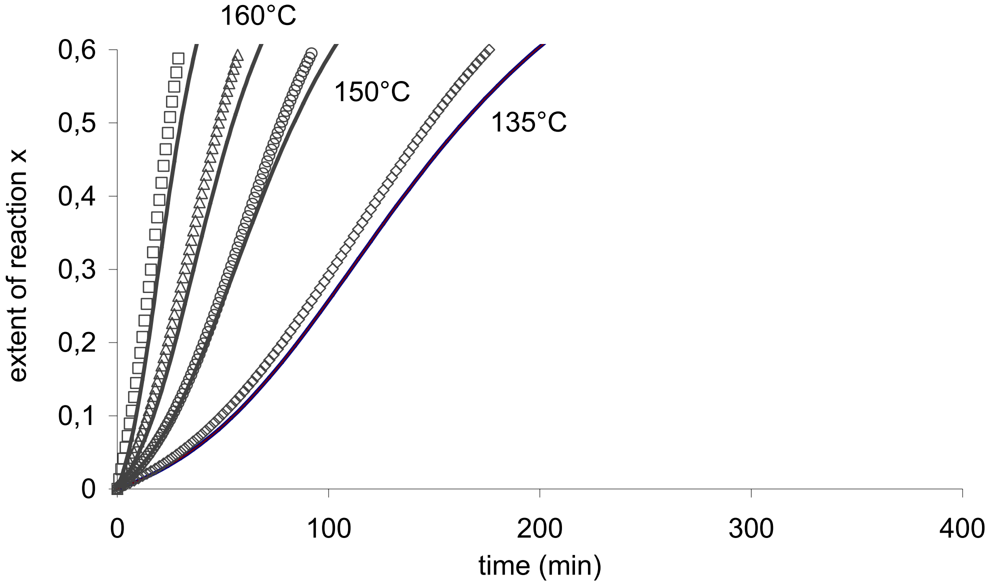


Fig. 3. Epoxy conversion vs reaction time at different cure temperatures for DGEBA/50%MCDEA-50%DDS. Experimental points at : (□) 175°C, (Δ) 160°C, (○) 150°C, (◊) 135°C ; Model prediction (——).

Dilution effect on the kinetics; presence of a thermoplastic (polyvinyl methylether, PVME)

The second part of the study is to understand phase separation of PVME in such systems using the model. PVME is first checked to be a non reactive additive therefore inducing only a classical dilution effect of the epoxide and amine functions, which results in a slight slowing down of reaction kinetics as it is seen for 10 wt% PVME blends crosslinked at 135°C in 10% or 50% DDS-MCDEA hardener formulations (Figure 4). In Figure 4, the model has been used to simulate the extent of reaction versus time at 135°C for 10wt% PVME systems. As our model tends to slightly underestimate the conversion, it happens to correctly fit the slight dilution effect with no change in the kinetic parameters. So it will be assumed to forecast reasonably well the reaction kinetics of all 10wt%PVME blends (whatever their DDS ratio), to evaluate cloud point conversions (and gel conversions) from measurements of cloud point times (and gelation times).

For the rest of the study, we will use the model of the neat system (Figure 5 and Figure 6). In order to further check this assumption, comparisons are given in Fig. 5 and 6 between the modeled kinetics of two matrices without PVME (50-50 or 10-90 mol%DDS-MDEA) and experimental kinetics of the undiluted and diluted (10wt% PVME) analogous systems. The agreement is satisfactory in the region of cloud point conversions (0.1 to 0.3).

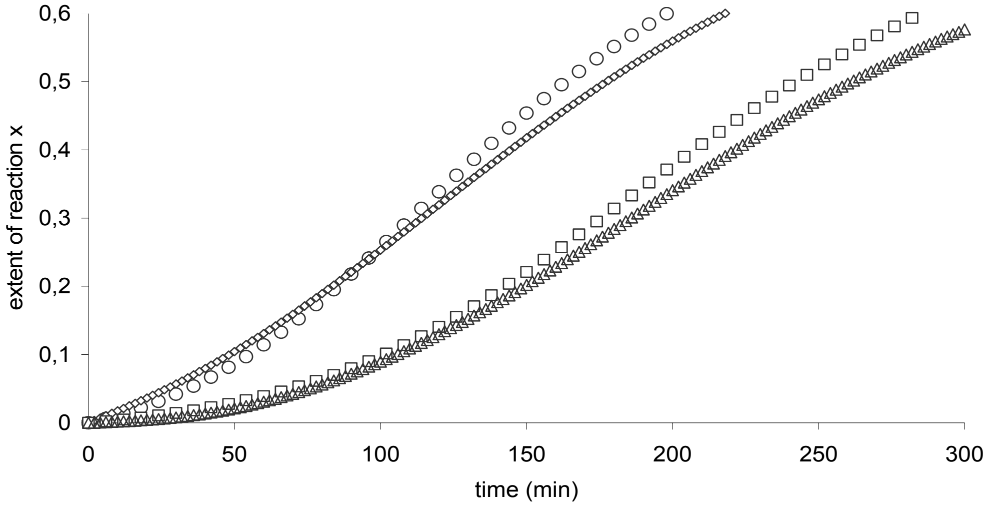


Fig. 4. Comparison of experimental data of extent of reaction and model data for two systems without PVME and diluted with 10%wt PVME at 135°C. (○) 50%DDS-50%MCDEA without PVME from model data; (◊) 50%DDS-50%MCDEA/10%PVME from experimental data; (□) 10%DDS-90%MCDEA without PVME from model data; (∆) 10%DDS-90%MCDEA/10%PVME from experimental data.

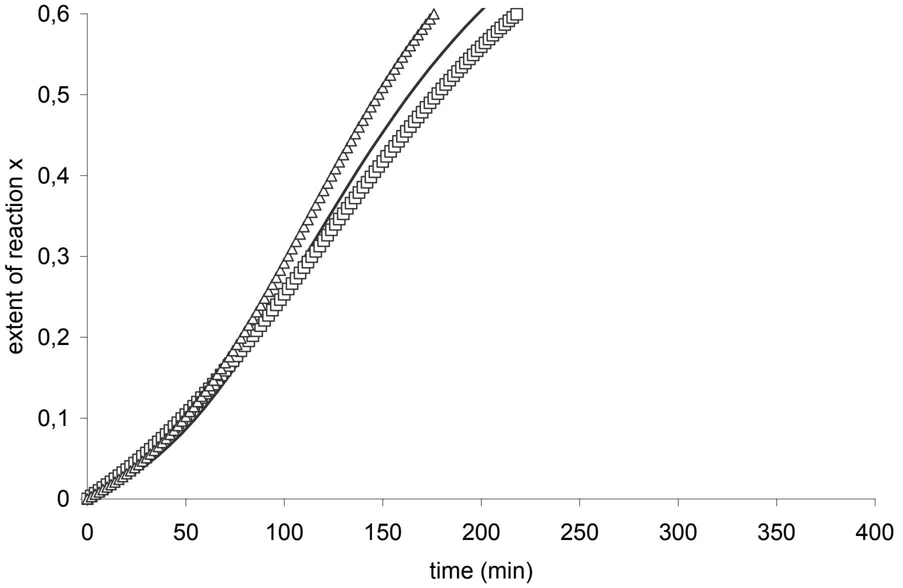


Fig. 5. Comparison of experimental data and model data for 50%DDS/50%MCDEA systems at 135°C. Experimental data: (∆) without PVME, (□) with 10%wt PVME ;(—–) model prediction.

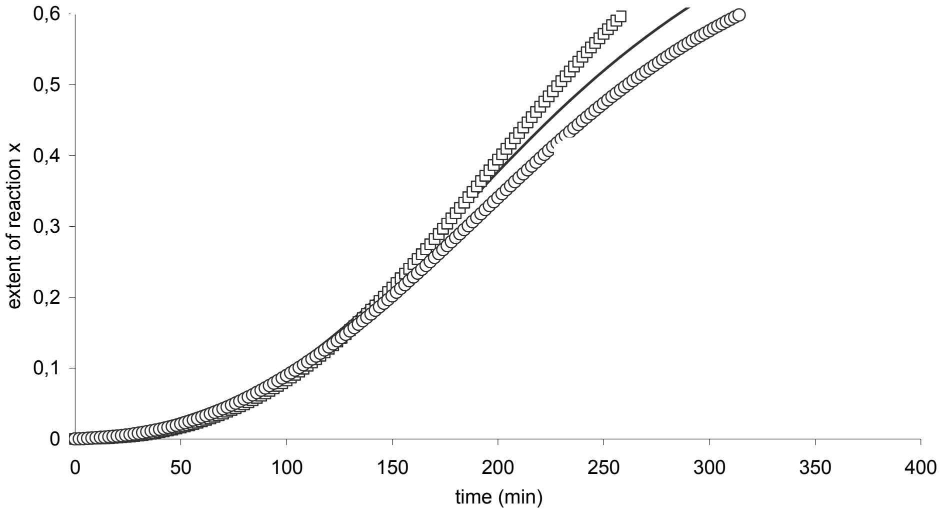


Fig. 6. Comparison of experimental data and model data for 10%DDS/90%MCDEA systems at 135°C. Experimental data: (□) without PVME, (○) with 10%wt PVME; (—) model prediction.

Conclusions

In this study we determined a kinetic model which is able to simulate the behaviour of an epoxy crosslinked with a mixture of two diamine. The kinetic parameter of this model was obtained by using pure one hardener/ one epoxy system and turns out to correctly model the kinetic behaviour of different proportions of hardener mixtures. The model seems to be in good agreement with the experimental calorimetric measurements. This epoxy/diamine system was then used in thermoset/ thermoplastic blend with PVME as a thermoplastic additive. The model used for the neat matrix shows a good correlation with the diluted matrix and allows us to know the composition of the mixture at cloud point conversion (when the phase separation occurs). The study of phase separation is presented in a second part.

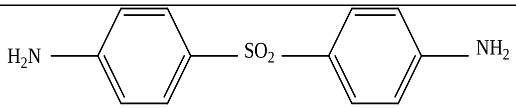
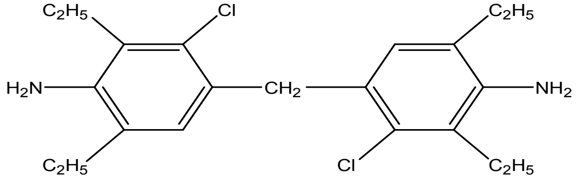
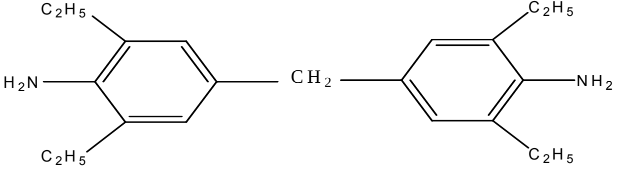
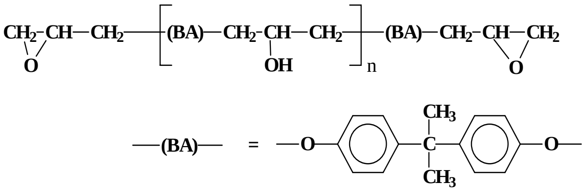
Experimental

Materials and sample preparation

The chemical formula and characteristics of the monomers used in this work are given in Table 2.

The diepoxide supplied by Dow Chemicals was a diglycidyl ether of bisphenol A (DGEBA) with an average degree of polymerization n = 0.03 and an epoxide equivalent weight of 174.25 g/mol. The two hardeners MCDEA (4,4’-methylenebis-(3-chloro-2,6-diethylaniline)) and DDS (4,4’-diaminodiphenylsulfone) were used as received from Fluka without further purification. Hardener(s)-DGEBA solutions or PVE blends are prepared at 80°C in a small reactor with a classical reactor stirring for five minutes in order to limit the extent of reaction at less than 2 %. The ratio of total amino hydrogen (NH) to epoxy functions is always kept equal to one but the molar ratio of DDS to MCDEA is varied from 0 to 100%.

Tab. 2. Chemical formula and characteristics of compounds used.

Name	Source	Chemical formula	f	Mn	Tf (°C)
4,4'Diaminodiphenyl sulfone (DDS)	Fluka		4	248	175
4,4'-Methylenebis-[3-chloro 2,6-diethylaniline] (MCDEA)	Lonza		4	380	92
4,4'-Methylenebis-[2,6-diethylaniline] (MDEA)	Lonza		4	310.5	88
Diglycidyl ether of bisphenol A (DGEBA) n=0,03	Dow Chem. (DER 332)		2	348.5	47
Polyvinyl methyl Ether (PVME)	Aldrich ref. 18,272-9	$\left[CH_2\text{–}CH(O\ CH_3) \right]_i$	-	32000	-

[f stands for functionality]

Differential Scanning Calorimetry

DSC scans (Mettler TA 3000) were carried out from -100°C to +330°C at 10°C/min to determine the values of the total heat of reaction ΔH_T corresponding to a conversion extent of 1 (x = 1). In the case of isothermal cures, a Perkin Elmer DSC7 apparatus was used.

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