



Kinetic of a thermoplastic-modified epoxy-aromatic diamine formulation: modeling and influence of a trifunctional epoxy prepolymer

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Abstract

The influence of a trifunctional epoxy prepolymer (triglycidylparaaminophenol, TGpAP) on kinetic reactions of a diepoxy prepolymer, diglycidylether of bisphenol A, DGEBA/diamine 4,4'-methylenebis[3-chloro 2,6-diethylaniline] MCDEA system was investigated as the influence of the addition of an initially miscible thermoplastic (polyetherimide, PEI or polyethersulfone, PES). The reaction mechanism between an amine and TGpAP is very complex so a phenomenological kinetic model is used. A reactive epoxy-amine system with TGpAP shows a faster reaction rate increase with temperature than a system containing only DGEBA because cyclization and etherification reactions are favoured with temperature in the case of TGpAP. A large discrepancy between theoretical value and experimental conversions at the gel point insoluble fraction was observed and can be explained by the fact that three epoxy groups of TGpAP have quite different reactivities due to different structures and substitution effects and also by the fact that other side reactions as cyclizations tend to result in gelation conversions higher than those expected from Flory's equation. After vitrification, the glass transition temperature of systems containing TGpAP goes on, increasing significantly because of intermolecular etherification reactions. Before any phase separation, a nonreactive thermoplastic (polyetherimide) was found to have no influence on reaction rate whereas polyethersulfone with terminal reactive phenoxy groups was found to accelerate the reaction rate. Similar behaviors were observed after phase separation. © 2000 Elsevier Science Ltd. All rights reserved.

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1. Introduction

High-temperature epoxy systems are widely used for composite materials in industry where properties such

as high modulus, thermal stability, solvent resistance are required. However, the high level of crosslinking in epoxy networks leads to brittle materials. The incorporation of a thermoplastic (TP) initially miscible, which phase separates during epoxy/hardener reaction, has often been used as a way to improve the toughness of epoxy networks since the early 1980s [1,2]. The most studied thermoplastics for the modification of epoxy networks are polyethersulfone (PES) and poly-

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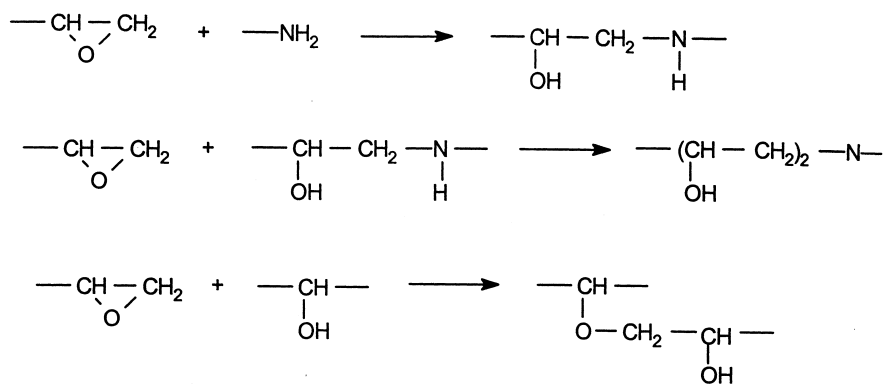


Fig. 1. Reactions between a DGEBA epoxy and a primary amine.

etherimide (PEI) [1–3]. It is interesting to know if they have an influence on the reaction rate and on structural transformations like vitrification and gelation on the epoxy/amine reactions.

In order to make composites by filament winding, miscibility at room temperature (25°C) and low viscosity of the system are required. For these reasons, a trifunctional epoxy prepolymer triglycidylparaaminophenol, TGpAP, is usually added to a classical diglycidyl ether of Bisphenol A (DGEBA) epoxy prepolymer/diamine system. TGpAP and tetraglycidyl dianiline (TGDDM) are the most used epoxy prepolymer derived from diglycidylaniline (DGA).

The reaction of DGEBA with primary amines is the most studied epoxy reaction because the mechanism, without any added catalyst, is usually simple [4–6]: it consists of reactions of amine hydrogens (primary and secondary amine) to epoxy groups and reactivities of

all epoxy groups are identical and independent [4–6]. At high temperature, etherification reaction may also occur (Fig. 1) [4–6].

On the contrary, the mechanism of DGA cured with primary amines is much more complex [7–14]. First, the reactivities of the epoxy groups in DGA derived molecules are not independent because of substitution effects. The proximity of the epoxy groups in DGA derived molecules also favoured intramolecular amine addition and intramolecular etherification (Fig. 2). Etherification is improved and becomes significant. So, where only two reactions are usually used to describe the reaction mechanism between a DGEBA derived molecule and a primary monoamine, Matejka et al. [9] showed that at least 12 reactions are needed to describe the reaction mechanism between a DGA epoxy and a primary monoamine.

DGEBA/diamine kinetics have been studied a lot. A

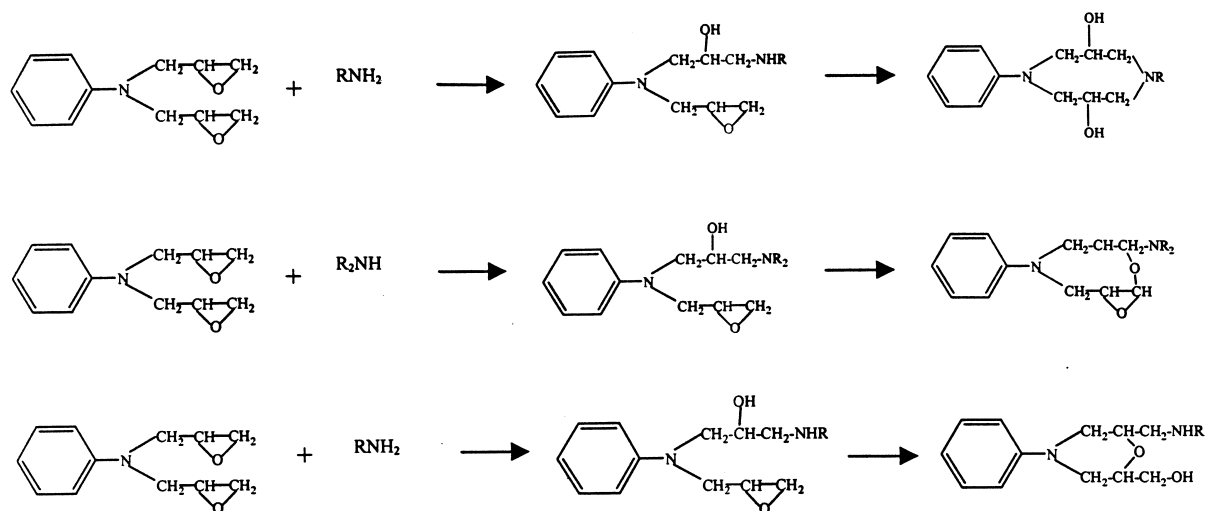


Fig. 2. Main cyclization reactions for DGA with a primary amine.

large range of models has been described. Riccardi et al. [15] proposed a mechanistically based model, which considers both the catalytic and noncatalytic mechanisms, etherification and also a different reactivity between secondary and primary amino hydrogens. Girard-Reydet et al. [16] applied this model with success to a DGEBA/4,4'-methylenebis[3-chloro 2,6-diethylaniline] (MCDEA) diamine system. Kinetics of TGpAP based system are evidently more complex.

The aim of this work is to predict and model the evolution of the epoxy conversion during curing, and to first study the influence of TGpAP on a DGEBA/amine reaction, and secondly the effect of two thermoplastics, a nonfunctional one (PEI) and a phenol terminated one (PES) on these systems. Due to the complexity of the reaction a phenomenological approach [17–19] is chosen.

2. Experimental

2.1. Materials

DGEBA (Dow Chemical, DER 332), TGpAP (Ciba-Geigy, MY0510) and an aromatic diamine 4,4'-methylenebis[3-chloro 2,6-diethylaniline] (MCDEA, Lonza) were used without further purification. Material purities were controlled by DSC and SEC. The thermoplastics used are a polyetherimide (PEI ULTEM 1000, from General Electric) and a polyethersulfone (PES 5003P, from Sumitomo). The PES has one phenol chain end. The chemical structures and characteristics of all species are listed in Table 1.

The epoxy prepolymers and the MCDEA were always used with a stoichiometric ratio amino-hydrogen to epoxy, $a/e = 1$. For all the modified systems, the thermoplastic is added in a 10% by total weight mixture to have continuous epoxy matrix morphology in post cured materials. In order to do composite by filament winding, in previous experiments we have established that it is necessary to add a 25% by epoxy weight of TGpAP to a DGEBA/PEI blend to have a miscible blend at room temperature. Neat systems are performed by mixing the epoxy prepolymers and the hardener at 90°C. For modified systems, the mixture is prepared by firstly mixing the epoxy prepolymers with the PEI at about 140°C to give a miscible blend. In the case of PES, it is necessary to proceed via solvent dissolution in a mixture containing 90% dichloromethane and 10% methanol. Dichloromethane/methanol solution is then evaporated under primary vacuum at room temperature. The diamine is finally added at about 90°C and mixed until the solution becomes clear. Samples reacted in glass tubes in an oil bath

kept at constant temperature (135 or 160°C). Table 2 summarizes the compositions of the systems used.

2.2. Techniques

A differential scanning calorimeter (Mettler TA300) was used to carry out the polymerization in the scanning mode at 10°C/min under argon, and to determine the residual heat of reaction in prereacted samples at 135 or 160°C. Extent of reaction, x , was calculated from the residual reaction heat, ΔH_{res} :

$$x = 1 - \frac{\Delta H_{\text{res}}}{\Delta H_{\text{max}}}, \quad (1)$$

where ΔH_{max} is the maximum reaction heat obtained from a DSC scan of an unreacted sample. For complex systems as there are different reactions with different heat, it would be better to speak of a degree of cure instead of an extent of reaction.

2.3. Method of modeling

The phenomenological model chosen has been developed by Kamal et al. [17,18] and has been used very often in the literature for many reactive systems including epoxy ones [19–22]. The kinetic can be expressed as a function of the concentration of epoxy groups $[e]$ and of hydroxyl groups $[\text{OH}]$ as follows:

$$-\frac{d[e]}{dt} = (k + k'[\text{OH}]^m)[e]^n, \quad (2)$$

where k and k' are the kinetic constants of the model having an Arrhenius behavior.

The epoxy conversion is $x = ([e]_0 - [e])/[e]_0$; with $[\text{OH}] = [\text{OH}]_0 + [e]_0 - [e]$ and $[\text{OH}]_0 = 0$. So the rate of conversion and the extent of reaction are related to one another as:

$$\frac{dx}{dt} = (K + K'x^m)(1-x)^n. \quad (3)$$

The relations between the apparent rate constants K , K' and the absolute ones k , k' are:

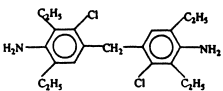
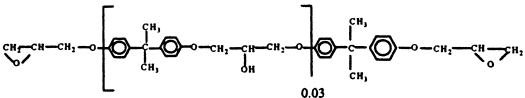
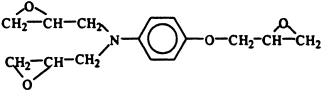
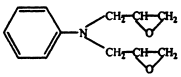
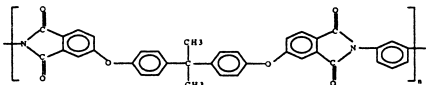
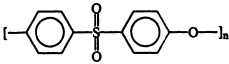
$$K = k[e]_0^{n-1}, \quad (4)$$

$$K' = k'[e]_0^{m+n-1}. \quad (5)$$

These apparent rate constants also depend on temperature according to Arrhenius' law:

$$K = A \exp\left(\frac{-E}{RT}\right), \quad (6)$$

Table 1
Characteristics of the system components

Reactant	Formula	Supplier
4,4'-methylenebis[3-chloro 2,6-diethylaniline] MCDEA (M)	 <p>$M=380\text{g/mol}$; $T_g=-8,8^\circ\text{C}$; $T_m=98^\circ\text{C}$; $\rho=1,14\text{ g/cm}^3$</p>	Lonza
Diglycidyl ether of bisphenol A DGEBA $\eta=0.03$ (D)	 <p>$M=348,5\text{g/mol}$; $T_g=-21,2^\circ\text{C}$; $\rho=1,17\text{ g/cm}^3$</p>	Dow chemicals DER 332
Triglycidyl para amino phenol TGpAP (T)	 <p>$M=300\text{g/mol}$; $T_g=-45,7^\circ\text{C}$; $\rho=1,22\text{ g/cm}^3$</p>	Ciba-Geigy MY0510
Diglycidylaniline DGA		
Polyetherimide PEI	 <p>$M_n=26000\text{g/mol}$; $M_w=50000\text{g/mol}$; $T_g=210^\circ\text{C}$; $\rho=1,27\text{ g/cm}^3$</p>	General Electric ULTEM 1000
Polyethersulfone PES	 <p>$M_n=21900\text{g/mol}$; $M_w=45990\text{g/mol}$; $T_g=220^\circ\text{C}$; $\rho=1,37\text{ g/cm}^3$</p>	Sumitomo 5003P

$$K' = A' \exp\left(\frac{-E'}{RT}\right), \quad (7)$$

where E , E' represent the apparent activation energy and A , A' are constants.

In the literature, sometimes m and n are imposed integer. Often $m = 1$ and $n = 1$ or 2 or even $m+n = 2$ [10,23,24]. As m and n represent the reaction orders, these hypotheses give a mechanistic aspect to the model. In agreement with previous work [15], we decide to fix $m = 1$ and $n = 2$. To obtain the theoretical values of x versus curing time, differential Eq. (3) is

resolved by Runge-Kutta method with K , K' as fitting parameters. Fitting is realized by minimizing the sum of the square error values between the experimental and calculated values of epoxy conversion. In order to validate the model, we compare the fitting values for the DGEBA/MCDEA system to those obtained with the use of a mechanistic model as described previously by Girard-Reydet et al. [16]. Modeling can be applied until vitrification. After vitrification, the reaction becomes diffusion controlled because the curing reactions are limited by slow diffusion of reactive functional groups and new parameters taking into account

the diffusion must be introduced in the model [25,26], but this aspect was within the scope of our project.

If the addition of a thermoplastic only leads to a dilution of reactive functions, the rate constants of the neat system (k_N , k_N') and the rate constants of the modified system (k_M , k_M') must remain the same. The apparent rate constants (K , K') depend on reactive function concentration and the epoxy concentration of the modified system $[e]_{0M}$ can be expressed as a function of the concentration of the neat system $[e]_{0N}$ by [19,25]

$$[e]_{0M} = \left(1 + \frac{w}{1-w} \cdot \frac{\rho_N}{\rho_{TP}}\right)^{-1} \cdot [e]_{0N}, \quad (8)$$

where w = mass fraction of additive; ρ_N = density of the epoxy/amine copolymer; ρ_{TP} = density of the thermoplastic.

This model can simulate the dilution of reactive functions and allows us to foresee if there is an influence of thermoplastic or not. Modeling is available only in a homogeneous medium, so until phase separation.

3. Results and discussion

3.1. Effect of TGpAP on kinetics

In order to understand the influence of the introduction of a trifunctional prepolymer on a diepoxy prepolymer/diamine system kinetic, three systems are studied: one containing only DGEBA as epoxy prepolymer (DM), another containing 25 wt% of TGpAP and 75 wt% of DGEBA (TDM) and the last one containing only TGpAP (TM). The detailed composition of these systems are gathered in Table 2.

Modeling is realized at two isothermal curing temperatures ($T = 135$ and 60°C). As explained previously, after vitrification modeling cannot be applied so only

experimental values before vitrification are involved in modeling. A system is considered to be at vitrification if its glass transition temperature equals at least the reaction temperature. The K and K' values obtained are phenomenological ones (Table 3), and the model does not allow to separate the effect of epoxy/amine reaction from etherification and cyclization reaction induced by the presence of TGpAP. In order to first validate our model, the fitting values for the DGEBA/MCDEA system were compared to those obtained with the use of a mechanistic model described previously [16]. The two fittings give quite the same values until vitrification (Fig. 3). Fig. 3 represents the experimental and simulated extent of reactions versus reaction time for the three neat systems: DM, TDM and TM for two different temperatures ($T = 135$ and 160°C).

At 135°C , the reaction rates are nearly the same for the three systems whereas at 160°C they are different. By increasing the curing temperature, the more the system contains TGpAP, the faster the kinetic is. This increase of reaction rate with temperature could be explained by etherification and intramolecular reactions that are favoured at higher curing temperatures in case of TGpAP based systems whereas with DGEBA based one these reactions can be neglected. By choosing the reaction orders as $m = 1$ and $n = 2$, the values obtained for the apparent activation energies are close to some results from the literature (104 instead of 80 kJ/mol and 72 instead of 60 kJ/mol).

Flory's equation predicts gelation conversion at $x_{\text{gel}} = 0.57$ for the DM system and at $x_{\text{gel}} = 0.40$ for the TM one. Experimental value of x_{gel} for the DM system is in agreement with theoretical value whereas for the TM one, the experimental value is higher than the theoretical one: 0.6 instead of 0.4. This large discrepancy can be explained by the fact that due to different structures and substitution effects, the three epoxy groups of TGpAP have quite different reactivities, and also by the fact that other side reactions as cyclizations

Table 2
System compositions

System name	TGpAP (T) (wt%) ^a	DGEBA (D) (wt%) ^a	MCDEA (M) (wt%) ^b	Thermoplastic (TP) (wt%) ^b
DM	0	100	35.3	0
TDM	25	75	39.3	0
TM	100	0	48.7	0
DMPEI	0	100	31.7	10
TMPEI	100	0	43.8	10
TMPES	100	0	43.8	10

^a Epoxy weight percentage by the whole epoxy weight.

^b Substance weight percentage by the whole blend weight.

Table 3
Kinetics parameters of neat systems

Reactive system	m	n	A (s ⁻¹)	A' (s ⁻¹)	E (kJ/mol)	E' (kJ/mol)
DM	1	2	14.4×10^9	1.99×10^4	108	46.5
TDM	1	2	10.2×10^9	16.9×10^4	107	53.5
TM	1	2	6.48×10^9	3390×10^4	104	72

tend to result in gelation conversions higher than those expected from Flory's equation.

The glass transition temperature of the DM and TM systems was followed as a function of cure time (Fig. 4). Classically, it is well known in DGEBA based

systems that when the transition temperature of the system reaches the curing temperature, the system vitrifies and chain mobility is reduced. Reactions can go on thanks to diffusion and the glass transition temperature ceases to increase significantly. This is what is

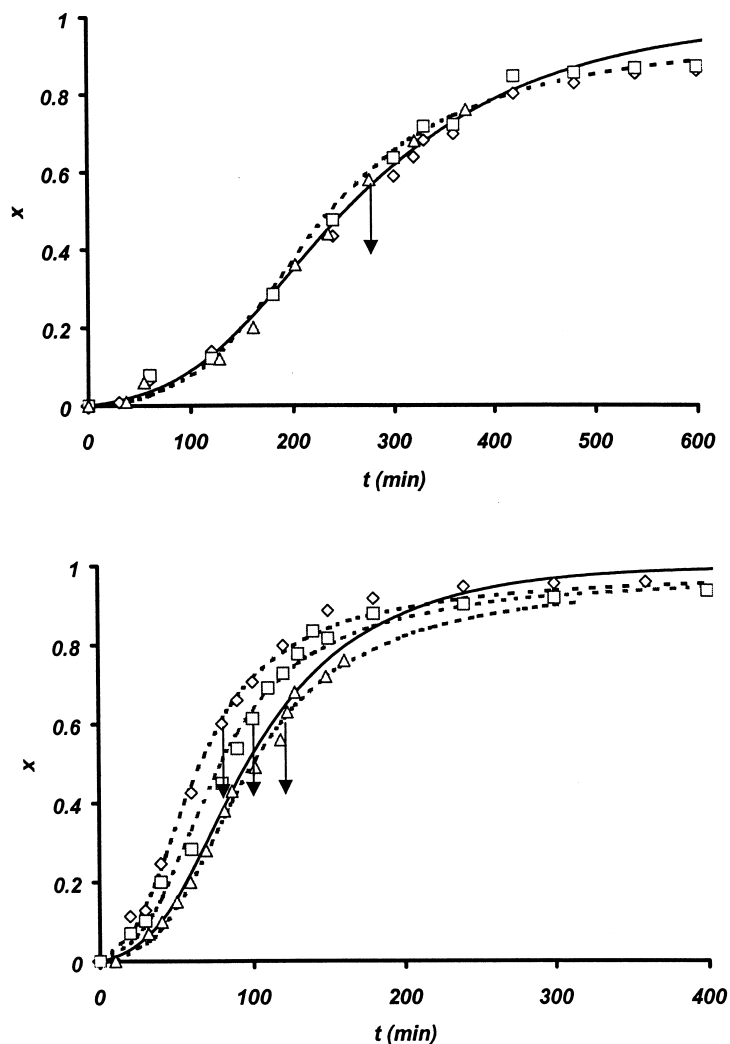


Fig. 3. Extent of reaction (x) versus reaction time (t) for different neat systems: \diamond , TM; \square , TDM; \triangle , DM; - - -, modeling curve; —, Girard-Reydet et al.'s [16] modeling curve for DM system. Different cure temperatures: (a) $T = 135^\circ\text{C}$; (b) $T = 160^\circ\text{C}$. Arrows (\downarrow) indicate gelation.

observed for the DM system. However, when the system contains TGpAP, after vitrification, the glass transition temperature goes on increasing above the curing temperature. A similar behavior has been observed by other authors [27]. This is believed to be due to the higher functionality of TGpAP having more reactive sites in close proximity so when the system vitrifies inter chain reactions or etherification can go on.

3.2. Thermoplastic effect on epoxy-amine curing reaction

The results discussed below concern only the TM system with PEI and PES as added thermoplastic (Fig. 5). The model takes into account the dilution

effect and in the case of PES we include the initial concentration of $[\text{OH}]_0$ due to the reactive PES end groups that can catalyse the reaction.

Phase separation happened more rapidly and at lower conversion in the case of PES than in the case of PEI ($x = 0.27$ and 0.6 for PEI which means close to gelation) (Fig. 5)

In the case of PEI, experimental measurements and simulation fit very well before phase separation occurred (Fig. 5). We can conclude that PEI has no effect on the epoxy-amine kinetic. After phase separation, the concentration in the two phases are unknown. A slight increase of reaction rate after the phase separation is observed. This effect has been

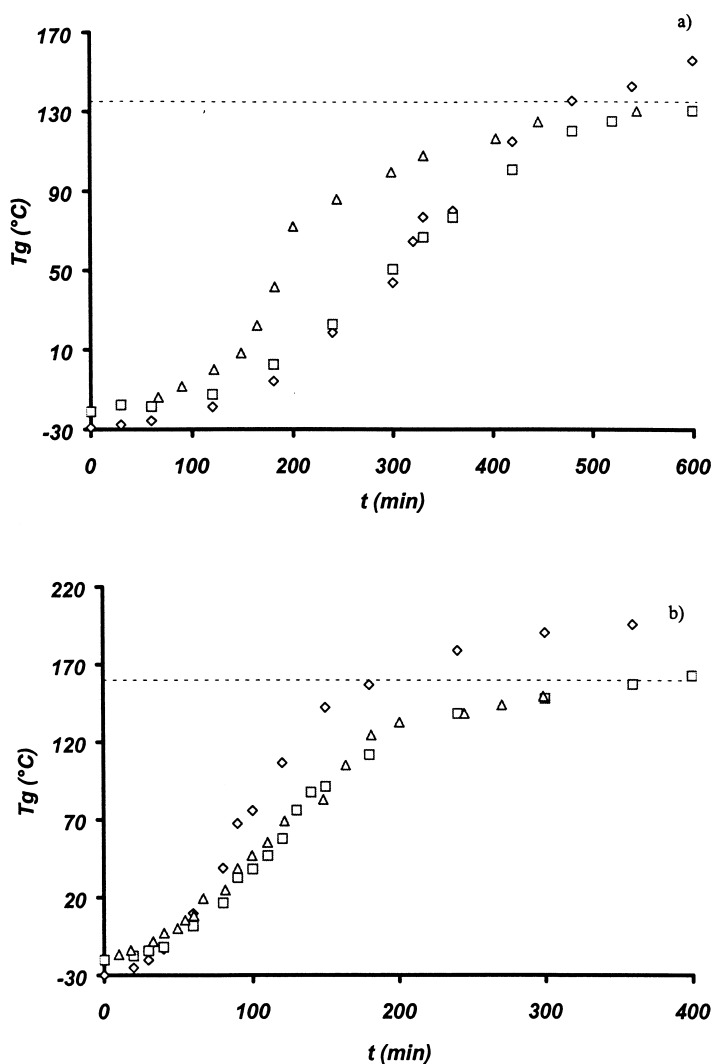


Fig. 4. T_g versus reaction time (t) for different neat systems: \diamond , TM; \square , TDM; \triangle , DM; ---, cure temperature. Different cure temperatures: (a) $T = 135^\circ\text{C}$; (b) $T = 160^\circ\text{C}$.

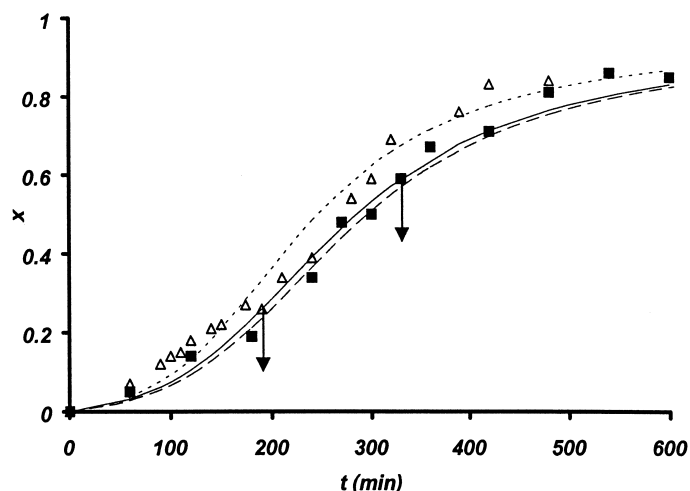


Fig. 5. Extent of reaction (x) versus reaction time (t) at 135°C for neat and modified TM system: ■, TMPEI experimental values; △, TMPES experimental values; ---, TM neat kinetic fitting; —, TMPEI kinetic fitting; —, TMPES kinetic fitting; arrows (↓) indicate cloud-point.

pointed out by Bonnet et al. [28] for higher concentration of PEI in DGEBA_{n = 0.15}/MCDEA/PEI systems and has been explained by an increase of epoxy concentration in the epoxy rich phase.

In the PES case, experimental measurements do not fit the simulated curve as well as in the PEI case (Fig. 5). The model does not take into account the reaction that can occur between the PES terminated phenol groups and the epoxy. It can be an explanation for the accelerated rate observed before phase separation. A similar fact has been observed with the same PES introduced in a cyanate ester system [29]. Before phase separation thermoset precursor kinetic is modified by thermoplastic additive only if it had reactive ended chain. Similar conclusions have been obtained for TDM systems.

4. Conclusion

The influence of a trifunctional epoxy prepolymer and of a thermoplastic additive on reaction kinetics of a diepoxy prepolymer/diamine system were investigated. Because of trifunctional epoxy prepolymer reaction with diamine is mechanistically very complex, a phenomenological model was used to predict the time and temperature dependence of the extent of reaction. For TGpAP based systems, a three reaction order was found to fit well with the experimental data. A large discrepancy between theoretical and experimental conversions at the gel point was observed and that can be explained by the fact that the three epoxy groups of TGpAP have quite different reactivities due to different

structures and substitution effects and also by the fact that other side reactions as cyclizations tend to result in gelation conversions higher than those expected from Flory's equation. The modeling includes concentration species so the dilution effect due to the addition of thermoplastic can be taken into account. Nonreactive PEI was found to have no influence on kinetic whereas PES with terminal reactive phenoxy groups was found to accelerate the reaction rate.

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