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KINETIC STUDY OF AN EPOXY SYSTEM BADGE (*n*=0)/1, 2 DCH MODIFIED WITH AN EPOXY REACTIVE DILUENT

M. Villanueva[1], *Lisardo Núńez*[1*], *M. R. Núńez*[1], *B. Rial*[1], *L. Fraga*[1] *and S. Montserrat*[2]

[1]Research Group TERBIPROMAT, Departamento de Física Aplicada, Universidad de Santiago, 15782 Santiago, Spain
[2]Departament de Màquines i Motors Tèrmics, Universitat Politècnica de Catalunya, Carrer de Colom 11, E-08222 Terrassa, Spain

Abstract

The curing reaction of an epoxy system consisting of a diglycidyl ether of bisphenol A (*n*=0) and 1, 2 diaminecyclohexane (DCH) with an epoxy reactive diluent vinylcyclohexane dioxide was studied by temperature modulated differential scanning calorimetry (TMDSC). The models proposed by Kamal and by Horie et al. were employed in the kinetic study. From these studies reaction orders, rate constants, and activation energies were determined. The technique of TMDSC allows to include in the kinetic study the effect of diffusion by means of the mobility factor, calculated from the curves of the complex heat capacity registered during the curing isothermal experiments. The results were compared to those obtained for the same system employing the reaction rate data.

Keywords: BADGE, epoxy reactive diluent, kinetic parameters, mobility factor, TMDSC

Introduction

Viscosity is a key factor in epoxy resin processing. Diluents are usually employed to reduce viscosity in order to aid general processability. Epoxy-based reactive diluents can participate, together with a resin and a curing agent, in polymerization and crosslinking reactions thus permitting the diluent to become chemically bound into the cross-linked network. In an attempt to preserve physico-mechanical properties at elevated temperatures, the use of a polyfunctional epoxy diluent has been considered.[1]

The use of this kind of additive, can originate modifications in the properties of an epoxy system during a curing reaction. In the case of a multifunctional epoxy reactive diluent, the behavior of the diluent is considered to be similar to that of the basic component and the crosslink densitiy seems not to be affected. The objective of this work was to study the curing kinetics of the system BADGE (*n*=0)/1,2 DCH modified with the multifunctional epoxy reactive diluent vinylcyclohexane dioxide (VCHD).

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[*] Author for correspondencec: E-mail: falisar1@uscmail.usc.es

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The chemistry involved in an epoxy curing process is rather complex and, in spite of the extensive research that has been done over the years, it is still not completely understood. As a result, it is impossible to describe it rigorously, and the existing models always involve certain assumptions and approximations.

The progress of the curing reaction is described quantitatively in terms of the degree of conversion of the epoxide groups, usually designated α. To model the kinetics it is necessary to derive an equation expressing the reaction rate, $\mathrm{d}\alpha/\mathrm{d}t$, as a function of α and the temperature T. The reaction rate of an epoxy system can be expressed by the sum of two mechanisms, n^{th} order and autocatalyzed.

For this study, two kinetic models were used to check the best fit to experimental data. One of them is the kinetic model proposed by Horie *et al.* [2], assuming equal reactivity for all the amine hydrogens. A general form of reaction rate for this model is:

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t}=(k_1+k_2\alpha)(1-\alpha)^{\mathrm{n}} \tag{1}$$

The other one is the kinetic model proposed by Kamal [3], that developed the following semiempirical equation:

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t}=(k_1+k_2\alpha^{\mathrm{m}})(1-\alpha)^{\mathrm{n}} \tag{2}$$

The introduction of the variable exponents m and n usually makes it possible to obtain a good fit to experimental data.

Experimental

Materials

The epoxy resin was a commercial BADGE (n=0) (Resin 332, Sigma Chemical Co., St. Louis, MO, USA) and the epoxy reactive diluent was vinylcyclohexane dioxide, with equivalent molecular masses of 173.6 g Eq^{-1} and 71.25 g Eq^{-1}, respectively, as determined by wet analysis. The curing agent was 1,2 diaminecyclohexane (DCH) (Fluka, Switzerland), with an amine hydrogen mass of 28.5.

Sample preparation

For calorimetric experiments, epoxy resin and diluent were carefully and homogeneously mixed before being added the curing agent at a stoichiometric ratio in respect to the total epoxy (BADGE plus epoxy diluent). The order of mixing was to prevent the start of reaction before the addition of the three components. The amount of diluent was of 15% of the total mass of mixture (BADGE/curing agent/diluent). In every case bulk samples of 200 mg were prepared. From the bulk samples, 6–8 mg in size were used for calorimetric experiments. The samples were sealed in pans, using a press, before introducing them into the calorimeter.

Calorimetric measurements

The temperature modulated DSC measurements were performed with a Mettler-Toledo 821e equipped with an intracooler, and STAR© software was used for alternating DSC (ADSC) evaluation, which is the TMDSC technique commercialised by Mettler–Toledo. The temperature and heat flow calibrations were performed using indium and zinc standards. The modulation conditions used in the quasi-isothermal curing reaction were an amplitude of 0.5 K and a period of 60 s. The non-isothermal ADSC experiments were performed at an underlying heating rate of 1 K min^{-1}, an amplitude of 0.5 K, and a period of 60 s. In order to calibrate the heat flow signal, correct the amplitude and eliminate the cell asymmetry, ADSC requires a blank with an empty pan on the reference side and an empty pan plus a lid on the sample side, at the same conditions as in the sample measurement. For ADSC measurements τ_{lag} was set to 0.

The DSC measurements were performed at the usual heating rates of 10 K min^{-1}. The sample mass was approximately 8–10 mg. All the calorimetric scans, TMDSC and DSC, were performed with a nitrogen gas flow of 50 mL min^{-1}.

Results and discussion

Kinetic study

At a first stage, DSC dynamic experiments were carried out to measure the total enthalpy change for this system. Knowledge of this enthalpy change is necessary for a subsequent isothermal study. The dynamic experiments were performed at a heating rate of 10°C min^{-1} between –60 and 300°C. From a second dynamic scan at the same heating rate, the $T_{g\infty}$ for this system was determined. The results of those experiments were the heat of curing of 493.6 J g^{-1}, and a $T_{g\infty}$ value of 173.0°C.

Table 1 Values of enthalpy changes from TMDSC isothermal measurements at different temperatures for the system BADGE (*n*=0) /1,2 DCH/ 15% VCHD

T/°C	ΔH/J g^{-1}
140	396.3
130	435.5
120	438.4
110	450.9
100	480.9
90	448.0
80	421.6
70	355.8
60	373.2

In the isothermal experiments, the modulation conditions were 0.5 K of amplitude and a period of 1 min. The temperature range was from 60 to 130°C during different periods of time depending on the experimental temperature. To determine the glass transition temperature corresponding to the isothermal curing, a dynamic experiment was performed, with the conditions of 1 K of amplitude, 1 min of period and a heating rate of 1°C min^{-1}. To make visualization of T_g easier [4], the amplitude in this second scan was bigger than in the isothermal experiment.

Enthalpy changes corresponding to the different selected temperatures were calculated as the total area under the total heat flow curves. These values are shown in Table 1. From these data, and the kinetic models used, values of the rate parameters can be determined.

Assuming a proportionality between the extent of the reaction and the heat evolved up to a time *t*, a general expression for the degree of conversion, α, can be written as:

$$\alpha = \frac{\Delta H_\mathrm{t}}{\Delta H_0} \tag{3}$$

where ΔH_t is the heat evolved up to a certain time, in an isothermal experiment, and ΔH_0 the total heat of reaction obtained from the dynamic experiments.

The reaction rate, dα/d*t*, was determined from the isothermal TMDSC experiments using the equation

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = \frac{\mathrm{d}H/\mathrm{d}t}{\Delta H_0} \tag{4}$$

assuming its proportionality to the heat flow d*H*/d*t*.

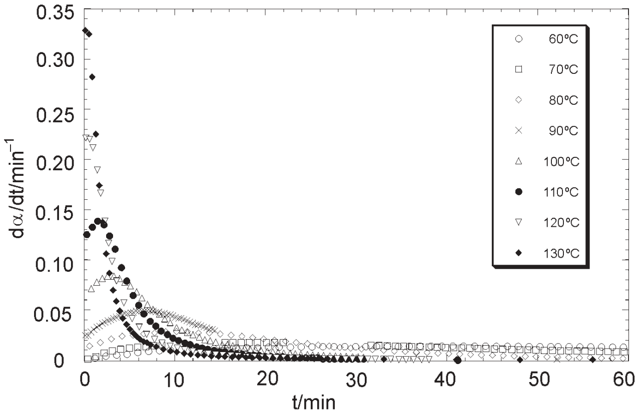

Fig. 1 Reaction rate *vs.* time plots for the different isothermal temperatures

Figure 1 shows the experimental reaction rates corresponding to the different isothermal temperatures. It can be seen that the reaction rate increases with temperature, but drops faster with increasing temperatures.

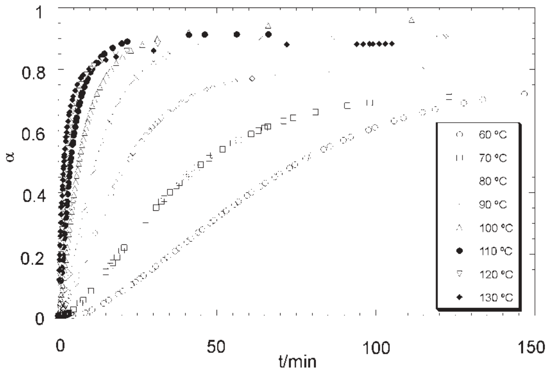

Fig. 2 Degree of conversion *vs.* time for the different isothermal temperatures

Figure 2 shows the experimental degree of conversion as a function of time for the different isothermal temperatures. It can be seen that the highest degree of conversion was achieved at the isothermal temperature of 100°C.

According to the models proposed by Horie *et al.* and Kamal [2, 3], the experimental reaction rate *vs.* α was fitted, considering the coefficients m, n, k_1, k_2 as fitting parameters. Table 2 shows the fitting of the experimental data to the kinetic models of Kamal and Horie *et al.*, with the corresponding correlation coefficients.

Table 2 Values of k_1, k_2, m and n for the system BADGE (n=0)/1,2 DCH/15% VCHD using Kamal model

T_c/°C	k_1/min^{-1}	k_2/min^{-1}	m	n	R
60	0.0060	0.021	0.38	0.94	0.9981
70	0.0037	0.042	0.41	1.72	0.9986
80	0.014	0.20	1.06	2.59	0.9962
90	0.023	0.22	0.90	1.92	0.9990
100	0.063	0.40	1.08	2.08	0.9999
110	0.12	0.89	1.31	2.34	0.9999
120	0.17	0.63	0.73	2.27	0.9982
130	0.32	1.42	1.02	2.78	0.9987

Except for 70 and 80°C, values obtained for m using the model proposed by Kamal [3] are very close to 1. This is the reason why all the other parameters (k_1, k_2, and n) have practically the same values that those obtained using Horie *et al.* [2] model that assumed m=1. For simplicity, only three temperatures (80, 100 and

130°C) were used for discussion and because values calculated using both models are very similar, the analysis will be carried out using only the less restrictive Kamal model.

Table 3 Values of k_1, k_2, and n for the system BADGE (n=0)/1,2 DCH/15% VCHD using Horie *et al.* model

T_c/°C	k_1/min^{-1}	k_2/min^{-1}	n	R
60	0.0099	0.047	1.53	0.9418
70	0.0078	0.12	2.67	0.9568
80	0.014	0.19	2.52	0.9961
90	0.024	0.26	2.04	0.9983
100	0.060	0.36	2.02	0.9999
110	0.11	0.55	2.05	0.9986
120	0.17	1.06	2.62	0.9996
130	0.31	1.47	2.81	0.9988

The activation energies corresponding to the two kinetic mechanisms were obtained from the Arrhenius plot of ln$k$ *vs.* 1000/T. Values of these activation energies are shown in Table 4. These values agree with those obtained for another similar systems [5–11].

Table 4 Values of activation energies and preexponential factors for the system with diluent using the Kamal and Horie *et al.* models

	Kamal model	Horie *et al.* model
E_a n-th order/kJ mol^{-1}	66.40±4.50	58.86±7.48
E_a autocatalytic/kJ mol^{-1}	61.94±7.90	50.80±3.57
A n-th order/s^{-1}	$1.93\cdot10^6$	$1.64\cdot10^5$
A autocatalytic/s^{-1}	$2.83\cdot10^6$	$8.93\cdot10^4$

Plots of the reaction rate *vs.* time, at the different isothermal temperatures, were made for the experimental data, Horie *et al.*, and Kamal models [2, 3]. Figure 3 shows that, for large curing times and at all temperatures, there is a deviation between the experimental data and the kinetic models. The reason for this deviation is that, from a given conversion, the curing reaction is no longer kinetically controlled, as it becomes diffusion controlled. To take account of this fact, a diffusion factor was included in the kinetic model. This effect was included through two different ways. The first one was made employing the ratio of the experimental reaction rate, obtained from the curve of the total heat flow, to the reaction rate predicted by the Kamal model, which does not account for diffusion (this model was used because is the one that considers less restrictions about the fitting parameters). The resulting data were fitted to the expression obtained from the fractional free volume theory and the approximations of Chern and Poehlein [12] and Rabinowitch [13] for the diffusion rate and chemical kinetic constants:

$$F(\alpha)=\frac{1}{1+e^{C(\alpha-\alpha_c)}} \tag{5}$$

where α_c is the critical conversion and C is a factor that depends on the temperature. For $\alpha<<\alpha_c$, $F(\alpha)$ tends to unity and the reaction is chemical kinetic controlled. As α

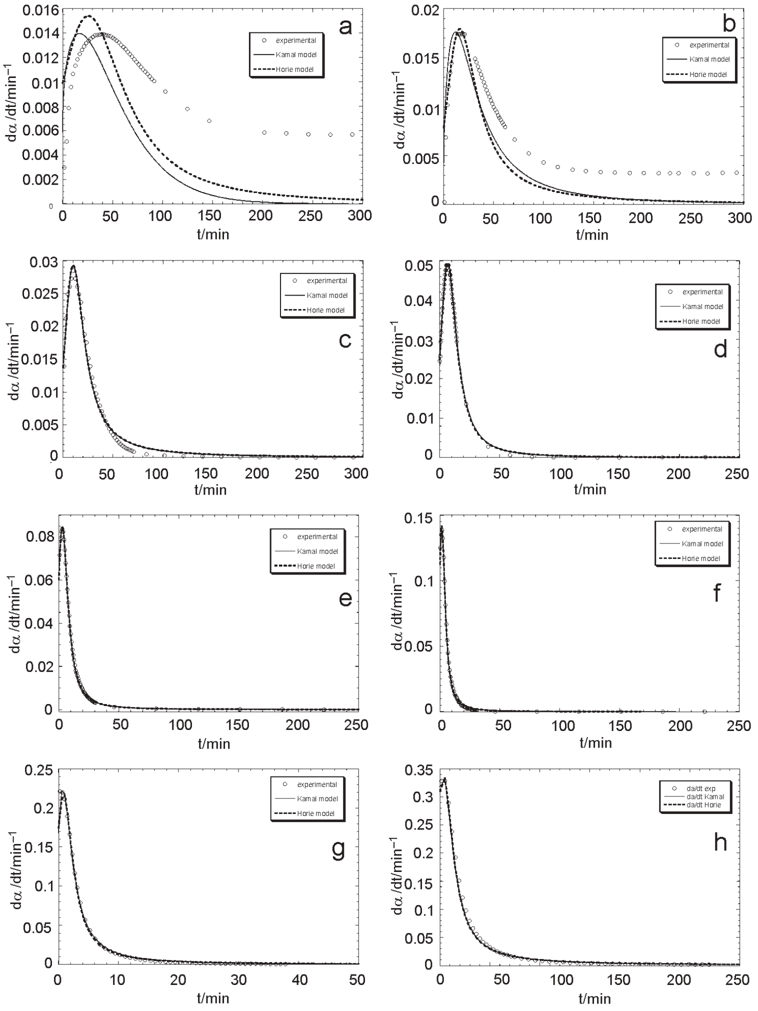

Fig. 3 Plots of reaction rate, dα/d*t*, *vs.* time, *t*. Comparison of experimental data with the Horie *et al.* and Kamal [2, 3] models at: a – 60°C; b – 70°C; c – 80°C; d – 90°C; e – 100°C; f – 110°C; g – 120°C; h – 130°C

approaches α_c, the diffusion factor begins to decrease. When the conversion reaches its critical value, α_c, $F(\alpha)=0.5$. For $\alpha>\alpha_c$, $F(\alpha)$ tends to zero and the reaction rate dramatically decrease and finally stops.

The values of the critical conversion (α_c) and C obtained by applying non-linear regression to $F(\alpha)$ *vs.* α data are listed in Table 5.

Table 5 Diffusion factor parameters for the system BADGE (n=0)/1,2 DCH/15% VCHD

T_c/°C	C	α_c	R
60	3.75	1.33	0.8740
70	24.60	0.76	0.9990
80	54.38	0.76	0.9966
90	88.47	0.88	0.9947
100	46.74	0.94	0.9813
110	124.19	0.89	0.9834
120	19.48	0.82	0.9894
130	27.89	0.79	0.9925

Using the diffusion factor, the reaction rate can be expressed in the following form to account for effects of diffusion:

$$\frac{d\alpha}{dt}=(k_1+k_2\alpha^{m})(1-\alpha)^{n}F(\alpha) \tag{6}$$

Another way to include the effects of diffusion in the reaction rate equation is through the mobility factor, *MF*. This factor is obtained taking into account the change in the heat capacity of the system during the curing reaction. Van Asche *et al.* (1995) [14] proposed the calculation of the mobility factor through the expression:

$$MF=\frac{c_p(t,T)-c_{p_g}(T)}{c_{p_l}(t,T)-c_{p_g}(T)} \tag{7}$$

where $c_{p_g}(T)$ is the complex heat capacity of the glass, $c_{p_l}(t,T)$ is the complex heat capacity of the liquid, and $c_p(t,T)$ is the complex heat capacity at time t and temperature T.

The main problem to calculate the *MF* is the selection of the point where MF reaches its maximum (1) and mimimum values (0). To determine exactly these two characteristic points, the step in the c_p was calculated and the onset was associated to c_{p_l}. The point where c_p reaches its half initial (onset) value was considered as the middle vitrification point. Figure 4 shows the behaviour of c_p *vs.* time at different isothermal curing temperatures.

From the modulated isothermal experiments vitrification times were obtained, and the main aspect was that the vitrification can be considered as a phenomenon that takes place during a time interval and not at a definite point. In Fig. 5 the vitrification curves for the system are shown. Onset and endset vitrification curves correspond to the onset and

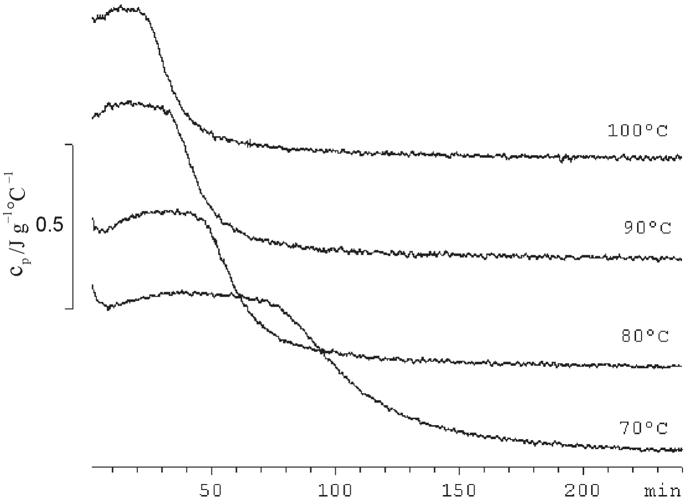

Fig. 4 c_p curves at the isothermal temperatures of 70, 80, 90 and 100°C

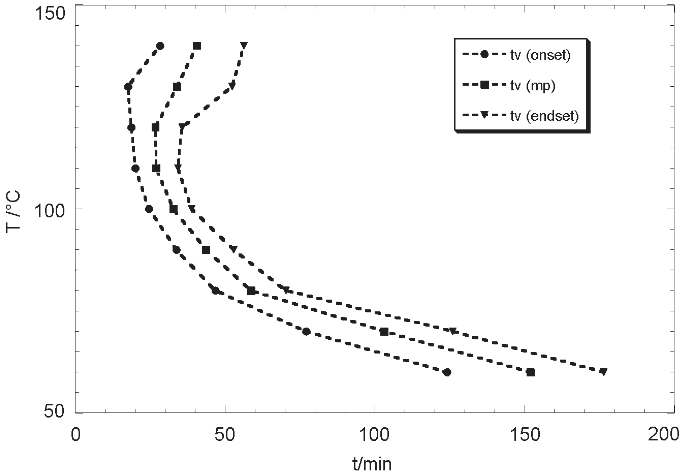

Fig. 5 Experimental vitrification curves for the system BADGE (*n*=0) /1,2 DCH/ 15%VCHD

endset points selected to calculate the midpoint vitrification time. As it can be seen, curves are 'S'-shaped as predicted by other authors for similar epoxy systems [15–22].

Figure 6 shows the reaction rate curves corresponding to experimental data, and those calculated using the model proposed by Kamal [3], with and without diffusion, and Kamal model including the mobility factor *MF* calculated as indicated before, at three different temperatures, 80, 100 and 130°C.

As it can be seen, the predictions of the theoretical model with diffusion differ depending on the diffusion factor included. There is not an uniform behaviour over

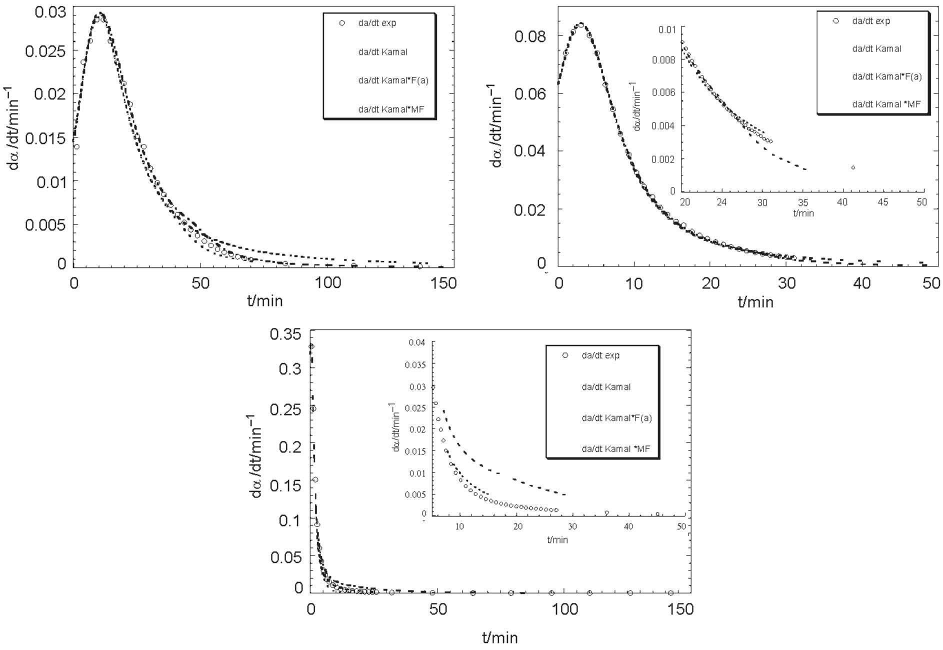

Fig. 6 Plots of reaction rate, dα/d*t*, *vs.* time, *t*. Comparison of experimental data with the Kamal model with and without diffusion factors (*F*(α) and *MF*) at the temperatures of: a – 80°C; b – 100°C and c – 130°C

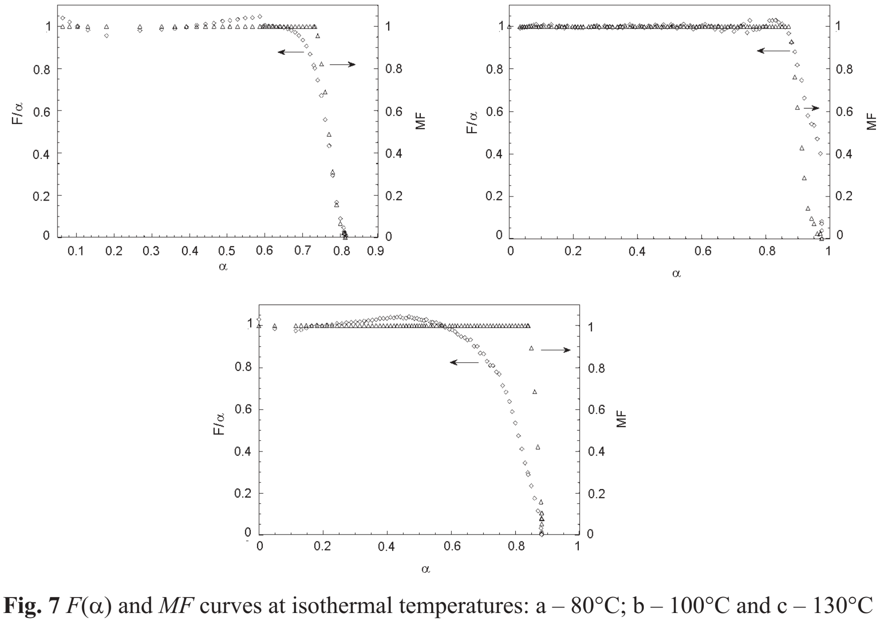

Fig. 7 *F*(α) and *MF* curves at isothermal temperatures: a – 80°C; b – 100°C and c – 130°C

the whole range of temperatures studied; in some cases the predictions based on $F(\alpha)$ are much better than those with *MF* and in other cases these predictions are very similar. Figure 7 shows the $F(\alpha)$ and *MF* curves for the different isothermal temperatures. It can be observed that $F(\alpha)$ decay is previous to the *MF* decay. This difference could be originated in the criteria used to select the initial and final points to calculate *MF*. Moreover, the decay in the mobility factor is very strong. Another factor for this difference could be the frequency of the modulated experiments. Some authors assert that the higher the frequency the lower the vitrification times [23], so if the frequency of the experiment is increased (period decreased), the decay in *MF* could start before and close to the $F(\alpha)$ decay.

Conclusions

The curing reaction of the epoxy system BADGE (n=0) /1,2 DCH/ vinylcyclohexane-dioxide was studied by modulated temperature differential scanning calorimetry. The kinetic study was based on the model proposed by Kamal, and also on the modifications of this model through the diffusion factor or the mobility factor obtained from the experimental values of the complex heat capacity. The differences observed using these three models do not allow a final conclusion about the best election but, in any case, there are some aspects that make TMDSC interesting. One of them is that vitrification time at a selected temperature can be calculated from an unique isothermal experiment (it is not necessary to make various partial isothermal experiments to determine the vitrification times) and other is that the effects of diffusion can be calculated without considering any theoretical model for the curing reaction rate.

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