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Influence of the accelerator concentration on the curing reaction of an epoxy–anhydride system [☆]

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Abstract

The effect of accelerator content on the curing reaction of an epoxy resin based on diglycidyl ether of bisphenol A (DGEBA) with methyl-tetrahydrophthalic anhydride was studied by DSC. The uncatalysed curing occurs at high temperature (between 190 and 310°C) with thermal degradation. The addition of accelerator which is a tertiary amine catalyst agent, namely dimethylbenzylamine (DMBA), causes two exothermic peaks. The cure extent and the position of the peaks depend on the accelerator content. The first peak, which is sharp and well defined, appears between 80 and 200°C and may be attributed to the catalysed curing. The second peak, which is broad, only appears for low accelerator content (lower than 1 pbw) in the zone of uncatalysed curing (between 200 and 320°C), and may be attributed to the uncatalysed curing.

The activation energy corresponding to the first exothermic peak in the catalysed curing, calculated by the Kissinger method, decreases with the accelerator content. Kinetic analysis performed by Málek's method shows that the autocatalytic model (two-parameter Šesták–Berggren equation) can describe satisfactorily the kinetics of the catalysed and uncatalysed curing. In the catalysed system, the parameters m and n increase slightly with the accelerator content, and the pre-exponential factor, $\ln A$, undergoes a slight decrease.

The maximum T_g of the fully cured epoxy obtained by isothermal curing at 110°C in catalysed systems shows no significant changes. These results mean that the differences observed in the kinetics of curing between catalysed systems do not imply significant changes in the structure of the network of the epoxy resin.

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1. Introduction

Interest in the curing of epoxy resins with different hardeners derives from the use of these materials as matrices in reinforced composites. In particular, the cure of diglycidyl ether of bisphenol A (DGEBA) with cyclic anhydrides yields thermosets which are widely used as insulating materials in the electrical industry.

At present, the uncatalysed reactions of epoxy resins and cyclic anhydrides are well known. According to the mechanism proposed by Fisch and Hofmann [1], the reaction occurs by consecutive step addition esterification involving carboxylic acid group intermediates and significant addition etherification as a side reaction [2–4]. In practice, however, the curing of epoxy–anhydride systems is performed with accelerating or initiating agents. Tertiary amines have been widely used as accelerating agents leading to a more complex mechanism than the uncatalysed curing. Tertiary amines participate in the formation of carboxylate and alkoxide ions originating an anionic alternating copolymerization [5], and practically eliminating the epoxide homopolymerization [6]. The crosslinking mechanism of catalysed epoxy–anhydride systems has been recently studied by different techniques: FTIR [7,8], NMR [2,5,8], and liquid chromatography and ozonometry [5].

Differential scanning calorimetry (DSC) has been used extensively to monitor and characterize the epoxy thermosetting systems cured by carboxylic acid anhydrides, amines and anionic or cationic catalysts [9]. The influence of the catalyst content has been studied in the cures of DGEBA/diamine/tertiary amine [10] and TGDDM/DDS/(BF_3: amine) [11]. The DSC traces show a multiple-peaked exotherm depending on the catalyst type, and its content. There are not many studies on this subject in epoxy–anhydride systems, with the exception of the work by Galy et al. [10].

The objective of this paper is to study the effect of the accelerator on the curing of DGEBA with methyl-tetrahydrophthalic anhydride. The accelerator was a tertiary amine catalyst agent, namely dimethylbenzylamine (DMBA). The non-isothermal DSC curves show two exothermic peaks whose position and intensity depend on the accelerator content. The first exothermic peak obtained at different heating rates yields information on the kinetics of the catalysed curing.

According to Málek's method for thermal kinetics [12], the determination of the activation energy allows the selection of the kinetic model and the calculation of the kinetic parameters of the curing reaction [13]. Results fit well to an autocatalytic model (two-parameter Šesták–Berggren equation), and the kinetic parameters were calculated. An increase in the accelerator content decreases the activation energy and changes the kinetic parameters of the curing reaction.

2. Experimental

2.1. *Materials and cure procedure*

The diglycidyl ether of bisphenol A (DGEBA)-based epoxy resin was Araldite F (CIBA-GEIGY) with an epoxy content of 5.3 mol kg^{-1}, determined by the hydrogen bromide method [14]. The hardener was derived from methyl-tetrahydrophthalic anhydride (MTHPA) (CIBA-GEIGY HY905) and the accelerator was *N*-dimethylbenzylamine (CIBA-GEIGY DY061). Resin and hardener were mixed at a weight ratio of 100:100 and then the mixture was stirred at room temperature for 20 min to obtain a homogeneous system. The required quantity of catalyst was added at the indicated concentrations of 0.25, 0.5, 1.0 and 2.2 parts by weight (pbw), mixed vigorously and then degassed in a vacuum oven at room temperature for about 15 min. Samples were enclosed in aluminium pans and introduced into the calorimeter to obtain DSC scans, or left in a thermostatic bath at a selected curing temperature for different periods of time to obtain isothermally cured samples of different extents of cure.

2.2. *Differential scanning calorimetry*

A Mettler thermoanalyser TA4000 equipped with a low temperature range DSC 30 differential scanning calorimetry module was used in the calorimetric measurements. The calorimeter was previously calibrated with indium standard. The sample weights were about 10 mg.

Non-isothermal scans were performed at different heating rates (2.5, 5, 10 and 20 K min^{-1}) from -80 to 380°C under nitrogen atmosphere in order to detect both the glass transition temperature (T_g) of the sample as mixed, and the exothermic heat of curing. After the first scan, the sample was cooled to 10°C at 20 K min^{-1} and, then, reheated up to 130°C at 10 K min^{-1} to determine the T_g of the cured epoxy.

The residual heat of curing and T_g were determined in the isothermally cured samples at a heating rate of 10 K min^{-1}. The degree of conversion α was calculated by the residual heat of curing [15]

$$\alpha = \frac{\Delta H_T - \Delta H_R}{\Delta H_T}$$

where ΔH_T is the total heat of curing obtained by a non-isothermal DSC scan of one fresh sample, and ΔH_R is the residual heat of curing of a sample isothermally cured at T_c during a specified period of time.

The kinetic analysis of the DSC data and the calculations were performed by the TA-SYSTEM software package [12].

2.3. *Thermogravimetric analysis*

Loss of weight was measured using a TG-50 module thermogravimetric analyser with a Mettler M3 microbalance coupled to a TA4000 Mettler Thermoanalyser. The hardener, resin and uncured samples were scanned by heating at 10 K min^{-1} from 50 to

Table 1
DSC results for the uncatalysed system at different heating rates β

β/(K min^{-1})	T^{a}_{sh}/°C	T_p/°C	ΔH/(J g^{-1})
2.5	-	218	364
5	220	240.3	356
10	230	264	338
20	250	290.5	324
40	260	322	308

[a] T_{sh} is the approximate temperature of the shoulder in the DSC curves.

600°C in nitrogen gas flow (200 ml min^{-1}).

3. Results and discussion

3.1. Curing of the uncatalysed system

The non-isothermal curing of the uncatalysed epoxy–anhydride system shows a broad exothermic peak between 190 and 310°C with a maximum at 264°C for a heating rate of 10 K min^{-1}. A small shoulder is observed about 230°C (Table 1). The DSC curves at different heating rates are shown in Fig. 1.

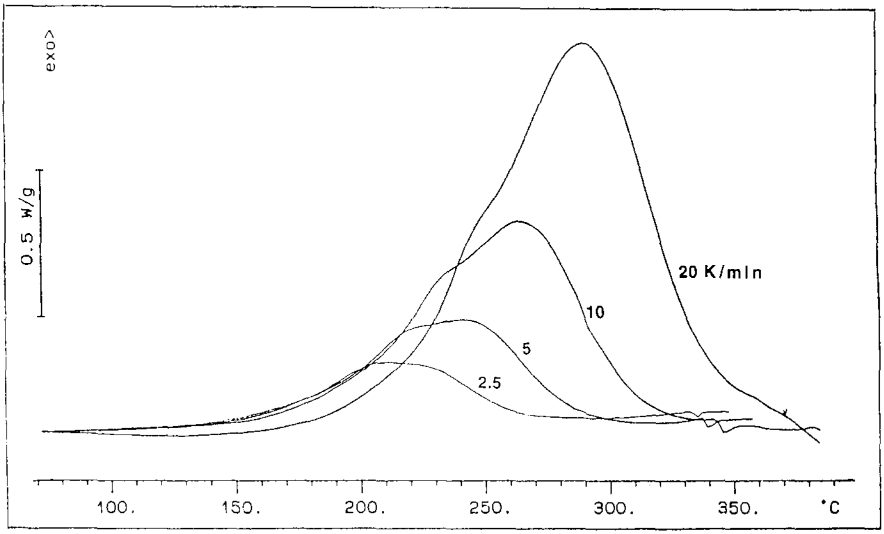

Fig. 1. DSC curves of the uncatalysed system at different heating rates: 2.5, 5, 10 and 20 K min^{-1}.

The thermogravimetric analysis shows a weight loss during the curing of the uncatalysed system. The TG curve (c) in Fig. 2 shows that the uncatalysed system experiences a weight loss of 25%, beginning at about 110°C with maximum weight loss rate at 195°C. Moreover, the hardener (TG curve (e) of Fig. 2) shows a weight loss starting at the same temperature as the uncatalysed system which suggests that the weight loss in this system corresponds to the unreacted hardener. The epoxy resin does not participate in this weight loss because its thermal degradation starts at 200°C when the reaction is in progress (TG curve (d) of Fig. 2). Galy et al. [10] have also observed a thermal degradation in a similar system.

The shoulder of the DSC exothermic peak has also been observed in some uncatalysed epoxy systems cured by diamine [10] as in DGEBA–isophorone diamine and DGEBA–cyanoguanidine, and was attributed to the different reactions of the primary and secondary amine group. In the present epoxy–anhydride system, the shoulder could be a consequence of the superposition of two thermal events: the endothermic heat from the weight loss of the hardener, and the exothermic heat generated in the curing reaction.

The addition of a small quantity of dimethylbenzylamine (DMBA) to the epoxy–anhydride system changes the position and shape of the DSC curves as Fig. 3 shows. This point will be discussed in the following section.

The DSC curves of the uncatalysed system scanned at different heating rates allow the calculation of the activation energy of the overall curing reaction by the Kissinger method [16], based on the equation derived from the condition for

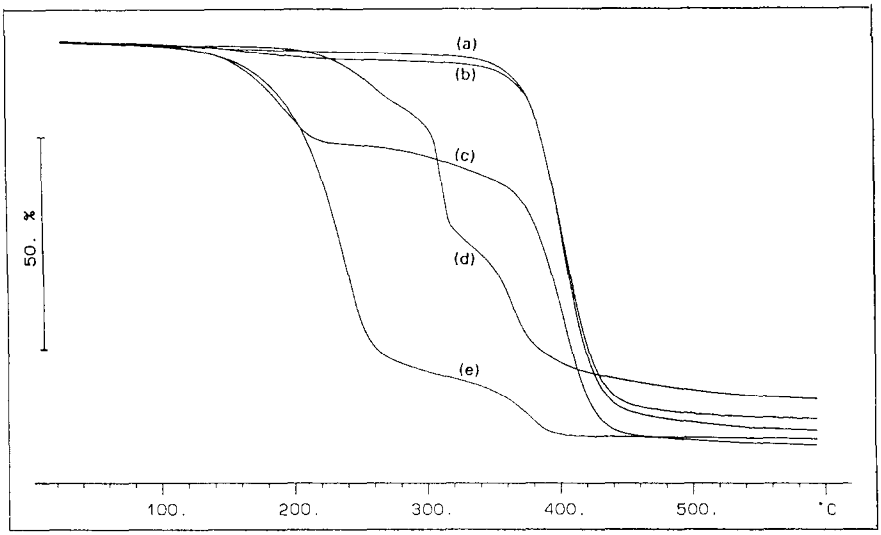

Fig. 2. Thermogravimetric curves of catalysed systems at accelerator contents of 1 pbw (a) and 0.5 pbw (b), uncatalysed system (c), Araldite F (d) and hardener HY905 (e). The heating rate is 10 K min^{-1}.

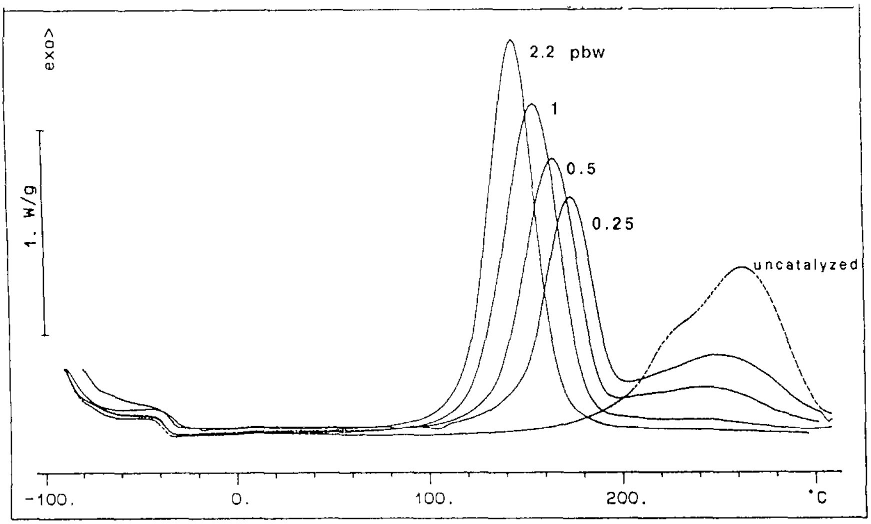

Fig. 3. DSC curves of catalysed systems at the indicated accelerator contents (0.25, 0.5, 1.0 and 2.2 pbw) and of the uncatalysed system, at a heating rate of 10 K min^{-1}.

the maximum rate on a DSC curve

$$\frac{d(\ln \beta/T_p^2)}{d(1/T_p)} = -\frac{E}{R} \tag{1}$$

where T_p is the peak temperature, β the heating rate, and E the activation energy. The calculated value of E is 56 kJ mol^{-1} for the main peak of the uncatalysed system, assuming that the sample weight remains constant during the curing.

3.2. *Curing of the catalysed systems*

The non-isothermal DSC curves of the catalysed epoxy–anhydride systems show a double exothermic peak (Figs. 3 and 4). At a heating rate of 10 K min^{-1}, the first peak appears sharp and well defined between 80 and 200°C depending on the accelerator content. The peak temperature (T_{p1}) decreases with the accelerator content (Fig. 3) and the same tendency is observed in both the initial (T_1) and final (T_2) onset temperatures. These values are summarized in Table 2.

The second peak becomes broader and flatter at higher temperatures, between 200 and 320°C. This peak only appears when the accelerator content is lower than about 1 pbw. This peak temperature can only be determined approximately because of its wideness and flatness. The values of the second peak temperature (T_{p2}) tend to decrease slightly with the content of the accelerator (Table 2). The second peak practically appears in the zone of the main peak of the uncatalysed system.

The overall heat of curing ΔH depends on the accelerator content and on the heating rate (Table 2). ΔH slightly increases when the heating rate decreases, as happens in

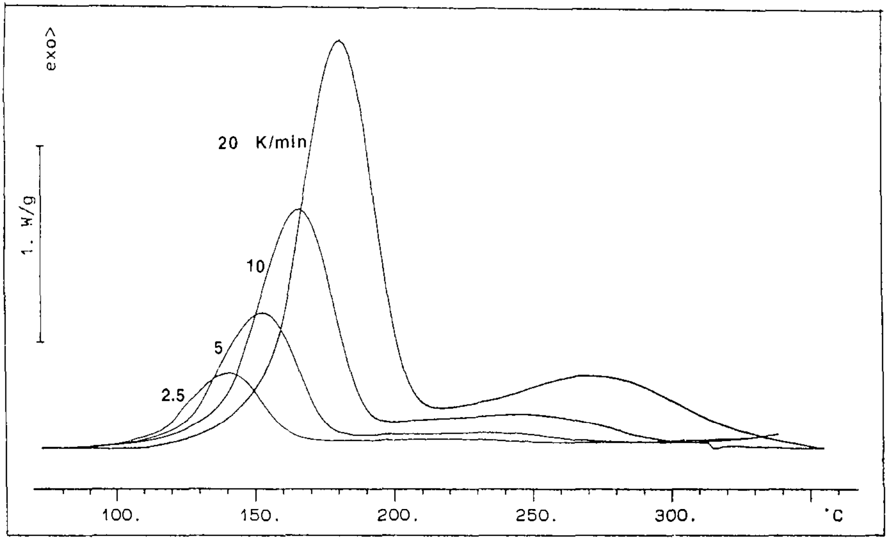

Fig. 4. DSC curves of the catalysed system with 0.5 pbw of accelerator at different heating rates: 2.5, 5, 10 and 20 K min^{-1}.

Table 2
DSC results for the catalysed systems at different accelerator contents *c* and heating rates β

c/pbw	β/(K min^{-1})	T_1/°C	T_{p1}/°C	T_2/°C	T_{p2}/°C	ΔH/(J g^{-1})
0.25	2.5	126	150.3	170	220	340
	5	138	162.2	181	238.6	342
	10	152	175.6	193	258	329
	20	168	191.4	208	282	313
0.5	2.5	115	141.7	162	–	344
	5	125	153.6	175	234	335
	10	139	166.8	188	245	314
	20	156	183.1	203	270	305
1.0	2.5	103	131.2	150	–	335
	5	113	143	164	–	336
	10	126	156.9	179	–	323
	20	142	172.1	194	245	301
2.2	2.5	94	120.1	137	–	331
	5	104	132.1	150	–	330
	10	117	146.3	165	–	329
	20	134	162.4	182	–	310

Key: T_1, T_{p1} and T_2 are the initial onset, peak and end onset temperatures, respectively, for the first exothermic peak.

T_{p2} is the peak temperature of the second exothermic peak.

ΔH is the total heat of curing.

some epoxy–diamine systems [10]. For a determined heating rate, ΔH tends to decrease with the accelerator content, but for heating rates of 10 and 20 K min^{-1} a slight increase of ΔH for an accelerator content higher than 1 pbw is observed.

For a given heating rate, the heat of curing corresponding to the first peak seems to increase with the accelerator content while the heat of curing of the second peak decreases, not being observed at 2 pbw of accelerator.

Thermogravimetric analysis shows that the main degradation process in catalysed systems starts at higher temperatures than in the uncatalysed system (Fig. 2). However, in systems with low accelerator content (0.25–0.5 pbw), a weight loss of about 5% can be observed between 100 and 250°C. The main degradation starts at 300°C (89–94% weight loss) with a maximum weight loss rate at about 405°C.

The activation energy calculated by the Kissinger method is shown in Fig. 5. the E value corresponding to the first exothermic peak of the catalysed curing decreases with the accelerator content.

The calculation of the activation energy for the second peak has only been performed for accelerator contents of 0.25 and 0.5 pbw (Fig. 5). This activation energy tends to increase with the accelerator content indicating an increase in the potential barrier of this reaction. The results obtained for the position and activation energy of these exothermic peaks presumably indicate that the first peak corresponds to the catalysed reaction and the second to the uncatalysed reaction. An increase of DMBA content

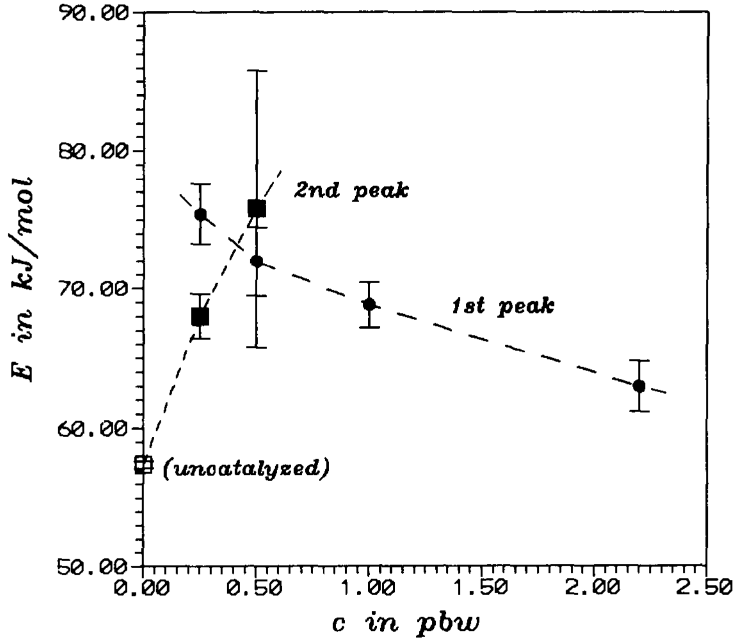

Fig. 5. The activation energy of the catalysed system for different accelerator contents calculated according to the first peak temperature (●) and the second peak temperature (■). The value of the uncatalysed system is also represented. Error bars correspond to the standard deviation.

accelerates the reaction and decreases the initial temperature of reaction and its activation energy. In addition, the area corresponding to the first peak increases and this indicates an increase of the extent of cure.

According to Matějka et al. [5], the tertiary amine (DMBA) is bound irreversibly to the intermediate products by the formation of a quaternary ammonium salt. Consequently, if the accelerator content is insufficient to complete the reaction corresponding to the first peak, a second exothermic peak will appear. This peak is attributed to the uncatalysed reaction whose molecular mechanism is different from the catalysed one [1–10]. In addition, the increase in the extent of cure corresponding to the first reaction brings about an increase in the number of crosslinks of the system so that the second reaction will be more difficult. This fact may justify the increase of the activation energy of the second peak.

3.3. *Kinetic analysis of the curing reaction*

The presence of two non-separate exothermic peaks brings additional difficulties in the kinetic analysis of the curing reaction. The first exothermic peak is separate from the second peak, allowing the selection of the beginning and end of the peak reaction. The kinetic analysis of the DSC data was performed by the method proposed by Málek [12]. The basic rate equation in the analysis of DSC kinetics at a given temperature is

$$\mathrm{d}\alpha/\mathrm{d}t = A\mathrm{e}^{-x} f(\alpha) \tag{2}$$

where $\mathrm{d}\alpha/\mathrm{d}t$ is the rate of conversion, A is the pre-exponential factor, $x = E/RT$ is the reduced activation energy, and $f(\alpha)$ is the function corresponding to the phenomenological kinetic model. In curing reactions, the most used functions are the reaction order model

$$f(\alpha) = (1-\alpha)^n \tag{3}$$

and the two-parameter autocatalytic model (Šesták–Berggren equation)

$$f(\alpha) = \alpha^m (1-\alpha)^n \tag{4}$$

For non-isothermal DSC curves, the change of conversion degree with temperature is

$$\frac{\mathrm{d}\alpha}{\mathrm{d}T} = \frac{1}{\beta}\frac{\mathrm{d}\alpha}{\mathrm{d}t} = \frac{A}{\beta}\mathrm{e}^{-x} f(\alpha) \tag{5}$$

where $\beta = \mathrm{d}T/\mathrm{d}t$. The following integral kinetic equation is obtained by separating the variables in Eq. (5), and integrating

$$\Delta H g(\alpha) f(\alpha) = \frac{E}{\beta R}\phi\left[\frac{\pi(x)}{x}\right] \tag{6}$$

where $g(\alpha)$ is the integral form of the kinetic model

$$g(\alpha) = \int_0^\alpha \frac{\mathrm{d}\alpha}{f(\alpha)} \tag{7}$$

where $\pi(x)$ is an approximation of the temperature integral which can be calculated by approximate expressions [12, 17], and ϕ is the heat flow generated in the curing reaction

$$\phi = \frac{d\alpha}{dt} \Delta H \tag{8}$$

ΔH being the total heat of curing.

According to Málek's method [12], all the kinetic parameters can be calculated from one non-isothermal DSC curve if the activation energy is previously known. The activation energy may be calculated from multiple scan methods by the Kissinger method, as mentioned before. To select the kinetic model which best describes the DSC data, the following functions should be adequately defined

$$y(\alpha) = \phi e^{-x} = \Delta H A f(\alpha) \tag{9}$$

$$z(\alpha) = \pi(x) \phi \frac{T}{\beta} = \Delta H g(\alpha) f(\alpha) \tag{10}$$

According to Eq. (9), the function $y(\alpha)$ is proportional to the kinetic model. The shape of the function $f(\alpha)$ is obtained by plotting the $y(\alpha)$ dependence normalized within the $\langle 0, 1 \rangle$ interval. If the $y(\alpha)$ function is decreasing monotonously having a maximum at $\alpha_M = 0$ (in practice, $\alpha_M < 0.05$), then the reaction order model can be used to describe the curing process. If the maximum of the $y(\alpha)$ function is localized in the interval $0.05 < \alpha_M < \alpha_p$ (α_p is the conversion degree at the maximum of the DSC peak), then the two-parameter autocatalytic model (Šesták–Berggren equation) will give the best description of the experimental data [12, 13].

The function $z(\alpha)$ has a maximum at α_p^∞ for a given kinetic model and is practically independent of the activation energy value. The α_p^∞ value corresponds to the maximum of a hypothetical DSC peak for $x_p \to \infty$. This parameter depends on the values of the kinetic exponents for both empirical models. Its value is very important for the kinetic model determination [12]. Once the kinetic model has been determined, the kinetic exponents and pre-exponential factor can be calculated by the method described in Ref. [12].

The DSC data for the first exothermic peak of the catalysed systems were converted to $y(\alpha)$ and $z(\alpha)$ functions according to Málek's method. These functions are shown in Figs. 6 and 7 for accelerator contents of 0.5 and 2.2 pbw and a heating rate of 10 K min^{-1}. For clarity, functions for other accelerator contents and heating rates are not included in these figures. The maximum values α_M of the $y(\alpha)$ function are between 0.24 and 0.35, and the α_p values range between 0.55 and 0.59. The α_p^∞ values are between 0.57 and 0.61. The average values of α_M, α_p and α_p^∞ determined from the DSC data at different heating rates are shown in Table 3. The shape of $y(\alpha)$ and the α_p^∞ values suggest that the autocatalytic model is more suitable than the reaction order model, which is in good agreement with a previously reported study on a catalysed epoxy–anhydride system [13].

For a given accelerator content, the exponents m and n were calculated for DSC data at different heating rates. The average values of m and n are shown in Fig. 8(a). Both

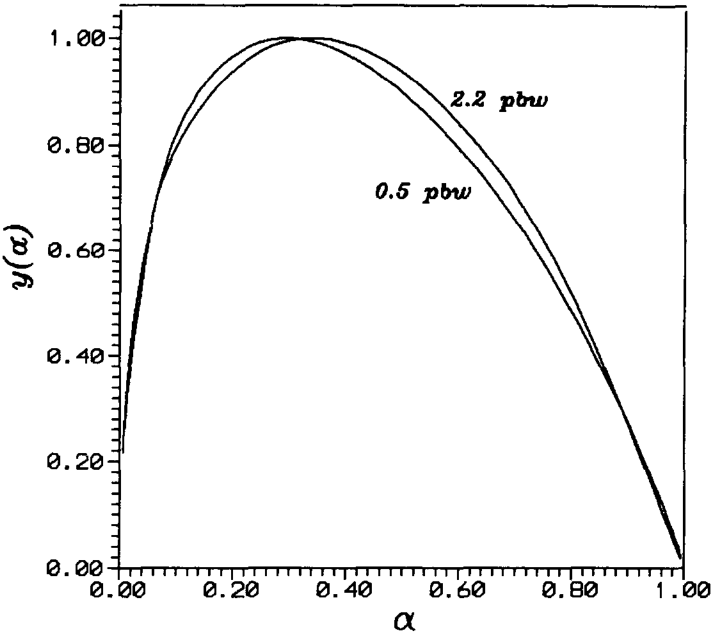

Fig. 6. The $y(\alpha)$ function of the catalysed systems at 0.5 and 2.2 pbw of accelerator for a heating rate of 10 K min^{-1}.

Table 3
Average values of the maximum of the $y(\alpha)$ function (α_M), the conversion degree at the maximum of the DSC peak (α_p), and the maximum of the $z(\alpha)$ function (α_p^∞) for different accelerator contents c

c/pbw	α_M	α_p	α_p^∞
0	0.21 ± 0.06	0.57 ± 0.08	0.62 ± 0.06
0.25	0.30 ± 0.06	0.56 ± 0.01	0.58 ± 0.01
0.50	0.28 ± 0.03	0.56 ± 0.01	0.58 ± 0.01
1.0	0.28 ± 0.02	0.57 ± 0.01	0.59 ± 0.01
2.2	0.33 ± 0.02	0.58 ± 0.01	0.60 ± 0.01

values are observed to decrease slightly when the accelerator content decreases. In the catalysed system, the average values of ln A decrease with the accelerator content (Fig. 8(b)).

Fig. 9 shows a very good agreement between the experimental DSC data (symbols) and the DSC curves calculated using the kinetic parameters (full lines) for different accelerator contents.

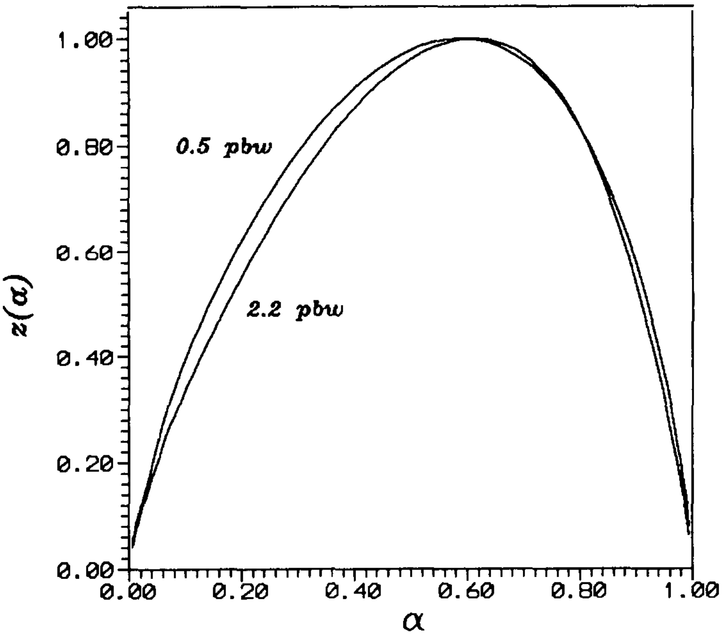

Fig. 7. The $z(\alpha)$ function of the catalysed systems at 0.5 and 2.2 pbw of accelerator for a heating rate of $10\,\mathrm{K\,min^{-1}}$.

The kinetic analysis of the uncatalysed curing was performed for the main peak, and only one broad exothermic peak was considered. The autocatalytic model was also found to be the most convenient to describe the non-isothermal DSC curves. The calculated values of m, n and $\ln A$ reproduce only the main peak, neglecting the shoulder which appears in the experimental DSC data. The average values of m, n and $\ln A$ are represented by open symbols in Fig. 8(a) and (b).

These results indicate that the introduction of a catalyst in the epoxy–anhydride system does not seem to change significantly the kinetic model, but that it does change the kinetics of the curing reaction.

3.4. *Maximum glass transition temperature*

The glass transition temperature is a parameter which gives information about the structure of the crosslinked epoxy. The T_g was measured in the second scan after a first scan where the sample was heated up to completion of the exothermic curing at about 380°C. The T_g values obtained by this method are plotted in Fig. 10 for different accelerator contents and, also, for the uncatalysed system. An increase of about 2°C in the T_g of the resin obtained by catalysed curing with respect to an uncatalysed sample is observed. This small difference could be attributed to the presence of homopolymer in the uncatalysed system where, according to Tanaka and Kakiuchi [6], the etherifica-

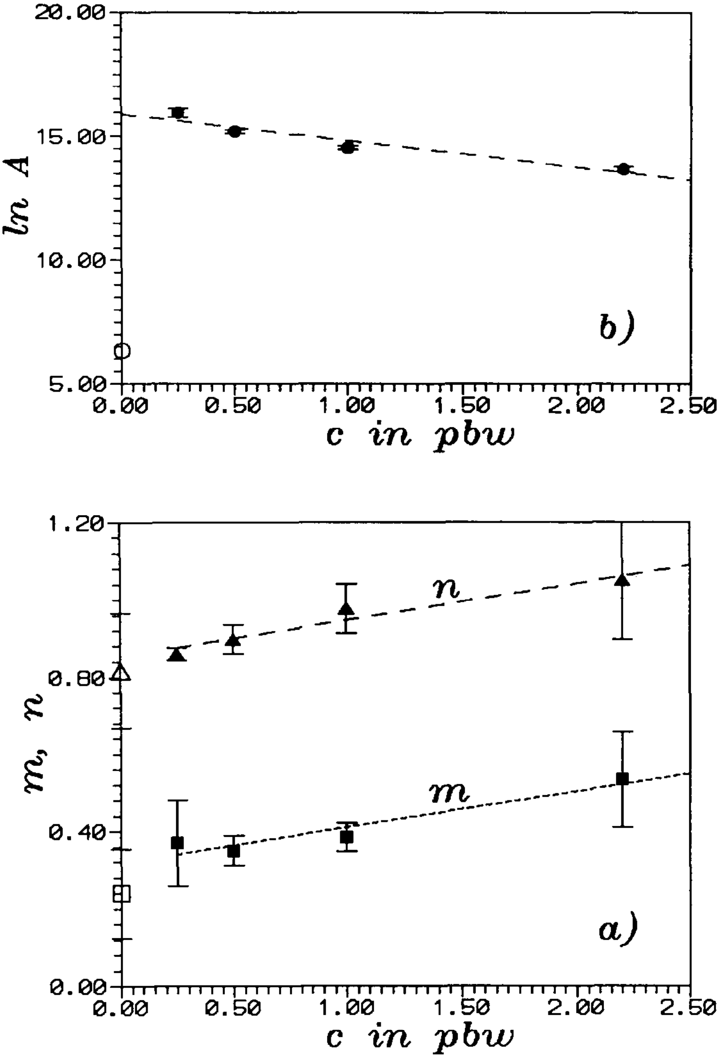

Fig. 8. The variation of the kinetic parameters with the accelerator content: (a) exponents *m* (■) and *n* (▲); (b) pre-exponential factor ln *A* (●). The lines correspond to a linear regression. The open symbols correspond to the uncatalysed system.

tion reaction is favoured in the absence of catalyst. The presence of homopolymer contributes to more flexible chains, lowering the T_g. Other authors [10, 18] have observed a more important change in T_g with the DMBA content in catalysed DGEBA–diamine as a consequence of the formation of new network structures.

In addition, the crosslinked epoxies obtained by non-isothermal curing, heating up to 380°C, may experience some thermal degradation. The thermogravimetric results

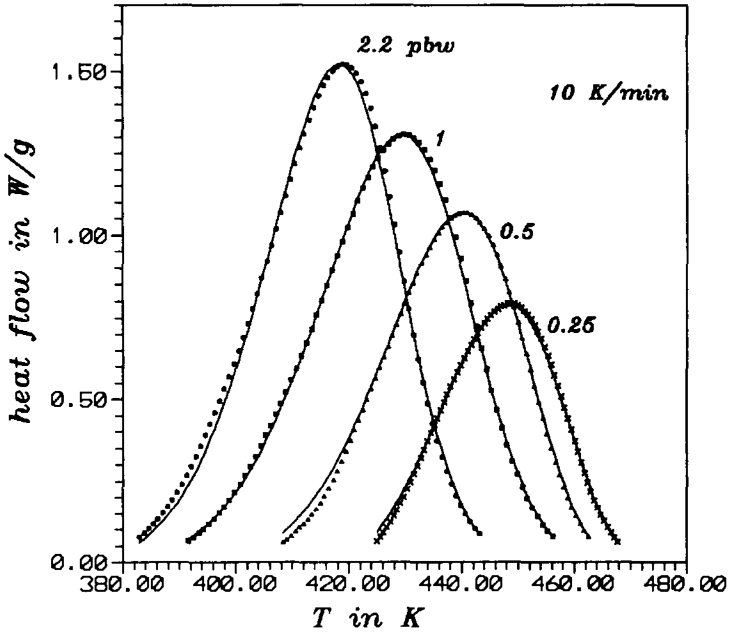

Fig. 9. Comparison of experimental (symbols) and calculated (full lines) DSC curves of different accelerator contents at a heating rate of 10 K min^{-1}.

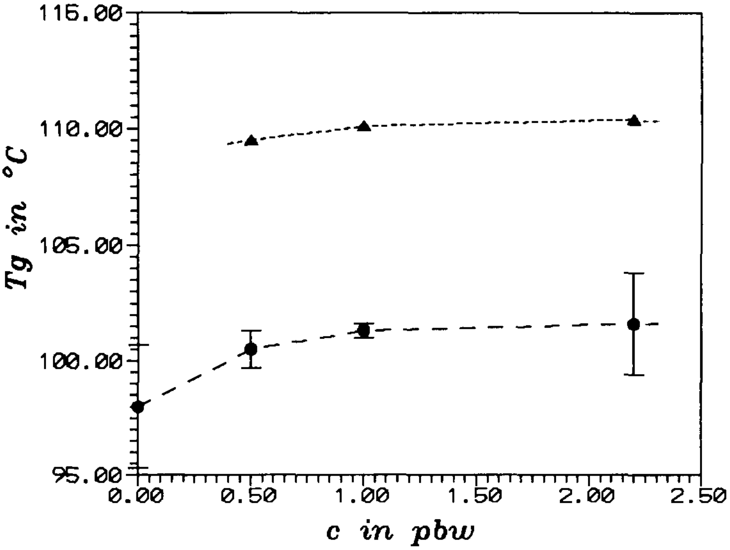

Fig. 10. Glass transition temperature obtained in the second scan (●) and the maximum glass transition temperature (▲) plotted against the accelerator content.

show that the main thermal degradation of catalysed and uncatalysed systems starts at about 360°C when the heating rate is 10 K min^{-1} (curves (a), (b) and (c) of Fig. 2). This process may cause a lowering of the T_g of the uncatalysed sample as well as of the catalysed ones.

The ultimate T_g of the epoxies can change depending on the curing history of the sample. In a previous work on catalysed DGEBA–anhydride systems [19], a difference of 14°C was found between the T_g obtained in the second scan after non-isothermal curing, and that obtained isothermally at a curing temperature T_c of 20°C above the maximum T_g. A similar effect was observed by Chang [20] in an epoxy resin.

In order to obtain the maximum T_g, the catalysed system was isothermally cured at 110°C for different curing times and, then, the samples were scanned at 10 K min^{-1}. The extent of cure was calculated by the residual heat of curing and the T_g was determined. When the extent of cure tends to one, the resin becomes practically fully cured and the maximum T_g is about 108–110°C (Fig. 11), with no significant differences. This means that the differences observed in the kinetics of curing between catalysed systems do not imply significant changes in the structure of the network of the epoxy resin.

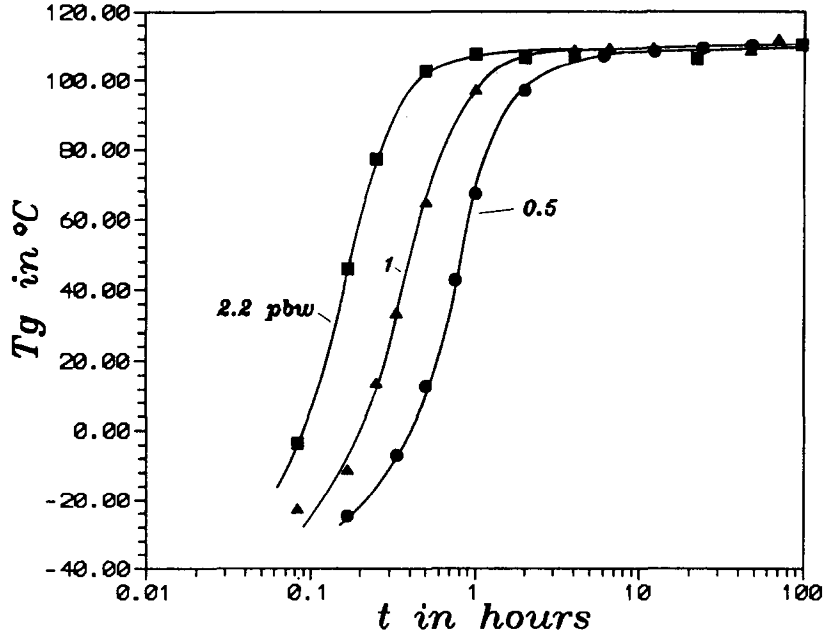

Fig. 11. Glass transition temperature of catalysed systems cured isothermally at 110°C for different times: 0.5 pbw (●), 1 pbw (▲) and 2.2 pbw (■). Lines are drawn as guides for the eye.

4. Conclusions

The effect of the accelerator content on epoxy resins based on diglycidyl ether of bisphenol A (DGEBA) cured by methyl-tetrahydrophthalic anhydride was studied by non-isothermal DSC. Confirmation has been found that the uncatalysed curing occurs at high temperature (between 190 and 310°C) with weight loss. The addition of the accelerator, which is a tertiary amine catalyst agent, namely dimethylbenzylamine (DMBA), yields non-isothermal DSC curves with two exothermic peaks. The extent of curing and the position of the peaks depend on the accelerator content. The first peak, which is sharp and well defined, appears between 80 and 200°C and may be attributed to the catalysed curing. The second peak only appears in the case of low accelerator content (lower than 1 pbw) in the zone of uncatalysed curing (between 200 and 320°C). This second peak may be attributed to the uncatalysed curing of the remaining epoxy–anhydride.

The activation energy calculated by the Kissinger method corresponding to the first exothermic peak of the catalysed curing decreases with the content of accelerator. The kinetic analysis was performed by Málek's method. Results show that the autocatalytic model (two-parameter Šesták–Berggen equation) can describe satisfactorily the kinetics of the catalysed and uncatalysed curing. The parameters m and n increase slightly with the accelerator content, and $\ln A$ shows a slight decrease.

The T_g determined in the second DSC scan of catalysed systems shows an increase of about 2°C with respect to the uncatalysed system. This is a small difference compared with the catalysed curing of epoxy–diamine systems. However, this difference could be attributed to the presence of homopolymer which is favoured in the absence of catalyst. The maximum T_g of fully cured epoxy obtained by isothermal curing at 110°C in catalysed systems shows no significant changes. This means that the differences observed in the kinetics of curing between catalysed systems do not imply significant changes in the structure of the network of the epoxy resin.

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