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# Influence of fillers and additives on the cure kinetics of an epoxy/anhydride resin

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## Abstract

The cure kinetics of a cycloaliphatic epoxy resin with and without additives and cured with an anhydride hardener was investigated by isothermal and nonisothermal differential scanning calorimetry (DSC).

Dynamic measurements were used to predict the total heat of reaction of the epoxy resin as well as its activation energy based on the methods of Kissinger and Ozawa. With these methods the inhibition and acceleration effects of additives and fillers on the kinetics have been demonstrated. Additives for advanced processing and property upgrade were added in less than 2 wt.%, whereas fillers on base of $SiO_2$ were incorporated in more than 50 wt.%. The effect of $SiO_2$ surface treatment was also objective of this study.

To describe the dependence of the conversion on time and temperature, isothermal DSC data were fitted to an autocatalytic model developed by Kamal and extended with a diffusion factor. The results show a very good agreement within the whole conversion range. Also the highly-filled system could be described very well by the phenomenological Kamal model.

*Keywords:* Kinetics; Resin; Calorimetry; Fillers; Additives

## 1. Introduction

Epoxy resins are extensively used as adhesives, coatings and matrices of high performance composite materials for components in automotive, aerospace and electronic applications. These advanced applications demand outstanding material properties of the epoxy resins that are predetermined by the chemical structure of the resin and hardener, as well as by the network achieved after curing. Thereby the curing conditions influence the network structure tremendously. Industrial applications require a complex property profile of the reacting and cured epoxy resin. For that reason almost all resins are modified with various additives and fillers to improve the processability and the mechanical, thermal and electrical properties in the cured state. The additives are usually added in a few weight percent (wt.%), e.g. to reduce the viscosity during casting, to suppress foaming, to avoid sedimentation of

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the fillers which may be present in high amounts (>50 wt.%). For industrial applications filler particles like layered silicates, $SiO_2$ or $CaCO_3$ are often used to reduce the price, but also to improve some mechanical and thermal properties of the product. Because of their high specific weight, the fillers tend to sediment in the resin. In order to prevent this effect, the fillers are usually surface modified (e.g. coated by functional silanes). Due to the functional groups of the modifier the inorganic particle may be incorporated into the organic network of the cured resin [1]. Inorganic additives and fillers are known to affect the cure kinetics of thermosetting polymers. They can change the network structure and affect the kinetics of the epoxy resin [2]. Additives are mainly surface-active substances and can act as inhibitors or accelerators with regard to the reacting system. On the one hand the surface of an additive may catalyse the reaction, on the other hand the reacting molecules can be catched and chemically linked to the surface of an aggregate (chemisorption). Thereby the cure reaction between resin and hardener is hampered or even inhibited. Another kind of inhibition may be due to sterical hindrance caused by the sorption of the reacting monomers on the surface of aggregates, fillers (physisorption). In order to trace exactly the structure-property-relationships for an epoxy resin system its cure kinetics has to be studied accordingly. This covers also the influence of additives and fillers. When modelling the cure kinetics of industrial processes, the curing rates at various temperatures and the activation energy of the reaction should be known to get a better control of the reactions and in consequence to optimize the physical properties of the final product. Cure kinetics of epoxy resins can be studied by different techniques, such as differential scanning calorimetry (DSC), infrared spectroscopy (IR) and dielectric spectroscopy [2]. In this work the DSC technique was used to investigate the kinetics of epoxy resins cured under isothermal and nonisothermal conditions.

The different methods to predict the cure reactions and kinetics were reviewed by Barton [3] and Duswalt [4] for different epoxy systems. The proceeding of conversion of the resin and residual heat of curing can be determined from isothermal and subsequent nonisothermal (dynamic) DSC scans [5]. The related data can also be used to draw the conversion rate as function of time and describe it by means of a suitable kinetic model. Nonisothermal scans allow us to calculate the activation energy of the resin system (Kissinger, Ozawa) and thus to get information about the rate of the reaction [6–8]. A large body of works was devoted to assess the cure kinetics of thermostes by using isothermal and nonisothermal DSC techniques. Most of the epoxy resins were studied on base of bisphenol A [8–19] with amines [9–13] and anhydrides [14–17], as curing agents. Note that the cure kinetics are different for each epoxy system. There are only few publications about the cure kinetics of cycloaliphatic epoxy resins [20,21]. The use of cycloaliphatic epoxy resins cured with anhydrides has a long history in the electronic industry (electric insulation, encapsulation). Interestingly, less information is available on their cure kinetics, especially when heavily filled, until now [1].

Kinetic parameters on the curing system are usually studied on systems containing mostly the resin and hardener. Systems relevant to practical applications are, however, far more complex as they contain many further ingredients, like accelerator, additives and fillers. Keenan pointed out that the true chemical reaction kinetics can hardly be described for a resin system of practical use. On the other hand, kinetic models can still be useful in providing empirical parameters for modelling and controlling the curing process [22].

The aim of this study is not only to give understanding about the cure kinetics of a system based on a cycloaliphatic resin (3,4-epoxycyclohexylmethyl-3′,4′-epoxycyclohexane carboxylate) and a mixture of anhydrides (methyl-hexahydrophtalic anhydride (MeHHPA) and hexahydrophtalic anhydride (HHPA)) as curing agent but also to investigate the influence of different additives and aggregates on the curing kinetics of the epoxy resin system. The activation energy and the effect of inorganic fillers as well as further ingredients on these values were studied under dynamic conditions. The latter were grouped in liquid and solid additives and filler (with and without silane surface treatment), as disclosed later. A further aim of this study was to describe the cure kinetics by the rate of cure and the degree of curing of the neat epoxy resin system under isothermal condition. The relevant results were compared with those achieved on an industrial relevant resin composition with the same base resin containing epoxysilane-treated filler and all above mentioned liquid and solid additives. Therefore it was important to find a mathematical expression for the cure kinetics that could be useful for FEM-simulations. Taking into account the exact mechanism of reaction was not the aim of this study.

## 2. Kinetic models

For studying the curing kinetics of thermosets three models were selected. Therefore nonisothermal and isothermal measurements were done in a conventional DSC. The dynamic kinetic methods are based on the equations of Kissinger [23,24] and Ozawa [25,26]. Isothermal studies supported an autocatalytic model which was found by Horie et al. [27] and developed by Kamal [28,29].

### 2.1. Dynamic kinetic model

A possibility to describe the kinetic effect of a cure reaction is given by their activation energy. A decrease in the activation energy means that less energy of the reacting components is needed to complete the reaction indicating an accelerating effect. It should be mentioned that the activation energy does not give any information about the mechanism of reaction only about its rate [30].

The activation energy, $E_A$, according to the Kissinger method, can be obtained from the peak temperature $T_P$, corresponding to the exothermal peak position of the dynamic scan. It is described as

$$\frac{\Delta\left(\ln\left(\frac{\Theta}{T_P^2}\right)\right)}{\Delta\left(\frac{1}{T_P}\right)} = -\frac{E_A}{R} \tag{1}$$

where $\Theta$ is the heating rate, $E_A$ the activation energy and $R$ the gas constant. Thus, the activation energy can be obtained from the slope of the plot of $\ln(\Theta/T_P^2)$ against $1/T_P$.

The equation of Kissinger is used by some authors to estimate the activation energy of reactions [8,10,16,31]. The model is not only applied to thermosets but also to thermoplastics. Li calculates the crystallization activation energy of a nonisothermal crystallization process of polyamide 10.12 [7].

Ozawa developed an alternative method to determine the relationship between activation energy $E_A$, heating rate $\Theta$ and peak exotherm temperature $T_P$ under the assumption that the extent of reaction at the exotherm peak is constant and independent on heating rate [6]. The equation is

$$\frac{\Delta\left(\frac{1}{T_P}\right)}{\Delta(\ln\Theta)} = -\frac{R}{1052\cdot E_A} \tag{2}$$

where $R$ is the gas constant.

Applying both models to obtain the activation energy, the results are very similar, but slightly higher values for the Ozawa model [8]. Duswalt found the calculated activation energy by the Ozawa method to be within a precision of ±3% [4].

### 2.2. Isothermal kinetic model

The distribution of heat of reaction H(t) for isothermal curing is given by

$$H(t) = \int_0^t \Phi(t)\,\mathrm{d}t \tag{3}$$

where $\Phi$(t) is the heat flow measured by the DSC experiment.

A basic assumption in the DSC technique is that during curing of thermosets, the heat evolution recorded is proportional to the extent of consumption of the epoxide group in the epoxy resin or the reactive group in the curing agent. That means heat of reaction $H(t)$ is proportional to the degree of conversion $\alpha(t)$

$$\alpha(t) = \frac{H(t)}{\Delta H_T} \tag{4}$$

where $\Delta H_T$ is the total heat of reaction of nonisothermal curing. Conversion at the end of isothermal cure $\alpha_{end}$ was calculated by subtracting the residual $\Delta H_R$ of the total heat of reaction $\Delta H_T$

$$\alpha_{end} = \frac{\Delta H_T - \Delta H_R}{\Delta H_T} \tag{5}$$

A general expression for the reaction rate as a function of temperature is

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t_R} = k(T)\cdot f(\alpha) \tag{6}$$

where $\alpha$ is the conversion and $\frac{\mathrm{d}\alpha}{\mathrm{d}t_R}$ is the rate of conversion. $f(\alpha)$ stands for a function of conversion which implies the reaction mechanism [3,32]. $k(T)$ is the rate constant of temperature and is assumed to be of Arrhenius-type:

$$k(T) = k_0\cdot\exp\left(-\frac{E_A}{RT}\right) \tag{7}$$

where $k_0$ is a constant, $R$ the gas constant and $E_A$ the activation energy.

The isothermal method can identify two types of reaction: *n*th order or autocatalytic polymerization.

The *n*th order model assumes that the reaction obeys the equation:

$$\frac{d\alpha}{dt_R} = k(T) \cdot (1 - \alpha)^n \tag{8}$$

Kamal [28] generated a mathematic model of an autocatalytic polymerization in order to predict the rate of conversion. The kinetic equation which is widely used in the literature for autocatalytic epoxy systems [8,9,11,14,17–19,31] was proposed by Kamal and Sourour [28,29]. The rate of conversion and the extent of reaction are related to one another as follows:

$$\frac{d\alpha}{dt_R} = (k_1 + k_2 \cdot \alpha^m) \cdot (1 - \alpha)^n \tag{9}$$

where $\alpha$ is the conversion of epoxy groups at time $t$. $k_1$ describes the rate constant of the reaction of order $n$ catalysed by an accelerator, $k_2$ is the rate constant of the autocatalytic reaction of order $m$.

At the beginning of a curing reaction the rate of reaction is dominated by the reactivity of the molecules. With raising degree of curing it becomes more and more diffusion controlled. So after gelation, when the flexibility of molecules is hampered in the glassy state, practically no full conversion (i.e. unity) can be reached. Therefore Fournier et al. [33] expanded the Kamal model by a diffusion factor $f_d(\alpha)$

$$\frac{d\alpha}{dt_R} = (k_1 + k_2 \cdot \alpha^m) \cdot (1 - \alpha)^n \cdot f_d(\alpha) \tag{10}$$

$$f_d(\alpha) = \left[\frac{2}{1 + \exp[(\alpha - \alpha_{end})/b]} - 1\right] \tag{11}$$

where $\alpha_{end}$ is the conversion at the end of isothermal cure and $b$ is an empirical diffusion constant of the material.

Other authors also used this or similar diffusion terms to the Kamal model in order to predict conversion rate also in the diffusion-controlled regime [8,12,14,31].

## 3. Experimental

### 3.1. Materials

All investigated systems were prepared from 3,4-epoxycyclohexylmethyl-3′,4′-epoxycyclohexane carboxylate, a cycloaliphatic epoxy resin (Araldit CY179) supplied by Huntsman (Basel, Switzerland). It has an epoxy equivalent concentration of 7.1 ee/kg. A mixture consisting of two commercial anhydrides, methyl hexahydrophthalic anhydride (MeHHPA) and hexahydrophthalic anhydride (HHPA), with an anhydride equivalent per weight of 6.25 ae/kg was used as curing agent. It was also supplied by Huntsman. The mass ratio of resin to hardener was 100:110, i.e. slightly away from the stoichiometric ratio.

In further formulations different aggregates were added to the initial resin system. Liquid additives cover a salt solution of unsaturated polyamine amides and acidic polyester as well as silicon rubber working as processing aids. Layered silicates, $SiO_2$-particles and carbon black were added as solid particles in order to prevent sedimentation of fillers. Altogether the solid additives were incorporated in low amount, viz. in less than 2 wt.%. Furthermore silicon rubber modifier was added in about 5 wt.% to improve the resistance of the formulation to stress cracking. Apart of the above additives the filled systems contained more than 50 wt.% fillers on $SiO_2$ base. These fillers were introduced with and without surface treatment. Surface treatment of $SiO_2$ was achieved by reacting with epoxysilanes during milling. Thereby the epoxysilane has been coated at the surface (also new one produced by milling) of the filler. The amount of this silane was adjusted to create a monomolecular layer on the $SiO_2$ filler via the known polycondensation reaction. These additional epoxy-groups are able to interact with the hardener thus the epoxysilanes can act as reactive sides. By extra epoxy-anhydride reactions the surface modified particles can participate in the network reaction so that the inorganic particle can be incorporated into the organic network. All components were supplied by Huntsman and used as provided.

### 3.2. Sample preparation

The resin was mixed with the additives and the fillers via stirring at room temperature and at 5 mbar pressure until a homogeneous mixture was formed. Different formulations were compounded (Table 1) and mixed with the hardener by stirring. Thereby the ratio of epoxy and anhydride groups was kept constant. Afterwards a vacuum of 1–5 mbar was applied for 3 min to degas the compounds. To measure the heat of reaction in DSC aluminium pans were filled with ca. 20 mg resin formulation and sealed.

Table 1
Epoxy resin systems with different contents of additives and fillers

| Formulation | Comp. A | Comp. B | Aggregate |
|---|---|---|---|
| A | Resin | Hardener | |
| B | Resin | Hardener | Liquid additives |
| C | Resin | Hardener | Liquid and solid additives |
| D | Resin | Hardener | Liquid and solid additives, modifier, fillers (surface modified) |
| E | Resin | Hardener | Liquid and solid additives, modifier, fillers (without surface-treatment) |

DSC measurements were carried out in a Mettler Toledo DSC 821$^e$ (Giessen, Germany) module equipped with an intracooler, and previously calibrated with high purity indium and zinc standards. Experiments were conducted in dynamical and isothermal modes. Runs at a constant heating rate were performed in a temperature range from −100 to 300 °C for each sample. The heating rates were set at 5, 10, 20 and 40 K/min, respectively. Kinetic studies were also performed with the DSC equipment working isothermally in a temperature range from 75 to 160 °C. The isothermal cure regime lasted between 30 min and 10 h depending on the curing temperature. The isothermal run was stopped when no signal of heat flow was detected. After the isothermal run all samples were quickly cooled to −100 °C with a cooling rate of 100 K/min. In a subsequent dynamic scan the sample was heated up to 300 °C at a heating rate of 10 K/min and the residual enthalpy and the glass transition temperature ($T_g$) were measured. All composites were made by the same resin/hardener ratio, i.e. all additives have been considered as inert (nonreactive) materials. The exact weight content of the fillers was controlled by thermogravimetric analysis (TGA) performed on a Mettler Toledo M3 (Giessen, Germany). TGA traces were recorded at a heating rate of 20 K/min from room temperature to 650 °C under nitrogen flux using the earlier tested DSC samples.

## 4. Curing of epoxy resins

### 4.1. Nonisothermal curing

To investigate the activation energy and the total heat of reaction, the heat flow at different heating rates of 5, 10, 20, 40 K/min was measured between −100 and 300 °C. Fig. 1 shows the results for the epoxy resin (A).

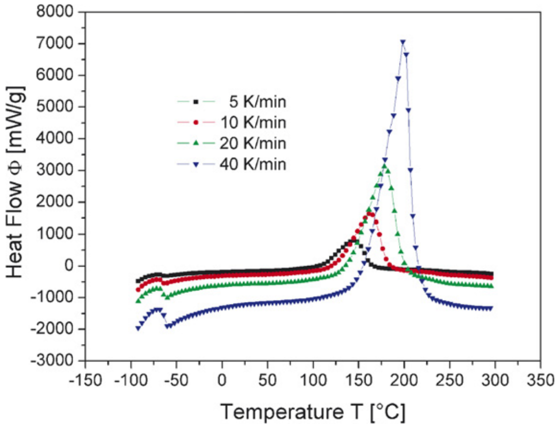

Fig. 1. Heat flow of the epoxy resin (Table 1: formulation A) as a function of temperature for nonisothermal curing at different heating rates (between 5 and 40 K/min).

As can be seen in Fig. 1 the $T_g$ of the uncured resin is at −65 °C and it does not change with the heating rate. $T_g$ was read at the inflection point of the endotherm step of the heat flow. The cure reaction is resolved as the pronounced exotherm peak in the heat flow curves. The initial cure temperature and the peak temperature $T_P$ increase with ascending heating rate. Due to this shift in $T_P$ the activation energy can be calculated by the Kissinger and Ozawa methods, respectively.

The peak temperatures obtained by nonisothermal measurements for the epoxy resin (A) at different heating rates (Fig. 1) are transformed according to the equations of Kissinger and Ozawa, respectively. In Fig. 2, the reciprocal temperature $1/T_P$ is plotted against the logarithm of the heating rate, $\ln \Theta$, based on the Ozawa method and, respectively, $(\ln \Theta/T_P^2)$ against $1/T_P$ following the Kissinger equation. From the fitted slope one obtains the activation energy, $E_A$, values which are 52.3 and 56.7 kJ/mol according to the Kissinger and Ozawa approaches, respectively. Both values are very similar, although the $E_A$ by the Ozawa method is slightly higher than that one calculated by the equation of Kissinger. Such difference was also noticed by other authors [8].

In Table 2, the dependency of the activation energy on the recipe formulation is shown. The activation energy of the epoxy resin without any additives and fillers (A) is 56.7 kJ/mol (Ozawa). $E_A$ increased when liquid additives (B) were added. $E_A$ further increased for the system C containing

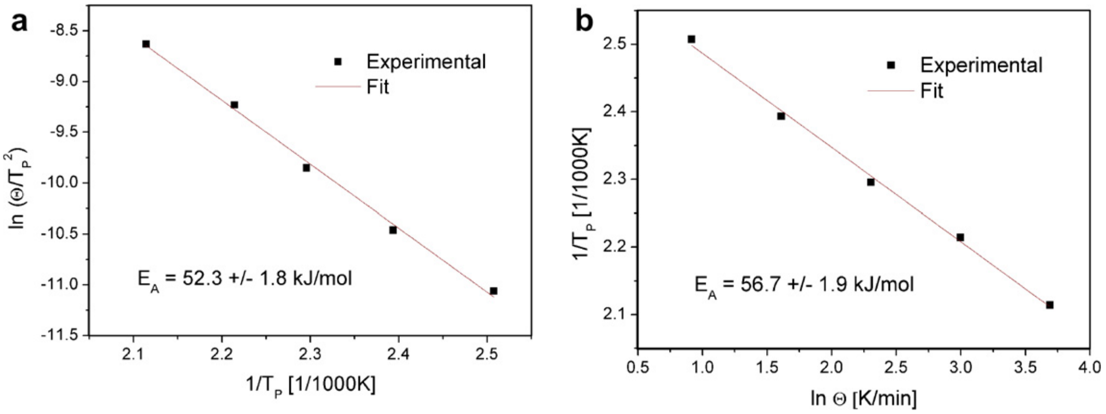

Fig. 2. Plots of $\ln(\Theta/T_P^2)$ versus $1/T_P$ (Kissinger) (a) and $1/T_P$ versus $\ln\Theta$ (Ozawa) (b) for the epoxy resin (Table 1: formulation A). Note: results deduced from nonisothermal DSC scans registered at different heating rates between 5 and 40 K/min.

Table 2
Activation energy of epoxy resin systems with different contents of additives and fillers

| Formulation | $E_A$ (Ozawa)/kJ/mol | $E_A$ (Kissinger)/kJ/mol |
|---|---|---|
| A | $56.7 \pm 1.9$ | $52.3 \pm 1.8$ |
| B | $63.3 \pm 1.2$ | $59.2 \pm 1.3$ |
| C | $67.2 \pm 0.9$ | $63.4 \pm 1.0$ |
| D | $59.2 \pm 1.5$ | $55.1 \pm 1.5$ |
| E | $66.9 \pm 2.8$ | $61.9 \pm 2.8$ |

additionally solid additives. By adding less than 2 wt.% liquid and solid additives the activation energy is increased of about 11 kJ/mol. So, adding any kind of the listed additives inhibited the reaction of the original epoxy resin. Interestingly, $E_A$ sharply decreased for the resin system containing all additives and surface-treated fillers (D). By contrast almost no reduction in $E_A$ was noticed for the companion system with nonsurface modified fillers (E). This result demonstrates that surface-treated filler accelerates whereas untreated filler practically does not affect the overall cure kinetics of the epoxy resins. Due to the surface treatment of the filler the corresponding inorganic particles may be chemically incorporated into the crosslinked organic network.

Additives are commonly mixed with the monomer in order to prevent premature reaction and increase the shelf life [34]. In our case the additives used not only favour the casting but also extend the storage life of the resin system. But compared to classical inhibitors, which raise the activation energy of about 20–30 kJ/mol in order to prevent early reactions, the effect noticed here is small.

Chu used the Ozawa method to determine the activation energy of epoxy resins highly filled with ceramic particles [35]. A possible reason for much higher values of the activation energy of the resin/hardener system based on diacrylate/mono acrylate, in comparison to literature values, is supposed to be the inhibiting effect of additives. They prevent the reaction and increase storage time [34]. On the contrary, ceramic particles showed a decrease in the activation energy and therefore an accelerating effect on the cure reaction. Prime reports that inorganic fillers usually affect the curing kinetics of thermosetting polymers [2]. Lem and Han [36] found that the activation energy of a commercial unsaturated polyester was reduced significantly (from 83 to 37.5 kJ/mol) when 50 wt.% of $CaCO_3$ was added. Other authors report no change for the activation energy of a commercial epoxy resin loaded with 8 wt.% carbon black [37].

Fig. 3 shows the total heat of reaction, as determined by time integration of the heat flow at nonisothermal curing, as a function of heating rate for the epoxy systems studied.

It is shown that the total heat of reaction of all investigated formulations varies within 380 and 460 J/g. The highest reaction heat that did not change significantly with the heating rate possessed the pure epoxy resin (A). Addition of any further components resulted in a reduction of the total heat of reaction. A significant decrease (of about 10%) was caused by the presence of liquid and solid additives (formulation C). On the other hand, additional incorporation of surface-modified fillers was accompanied with a relatively small reduction of the total

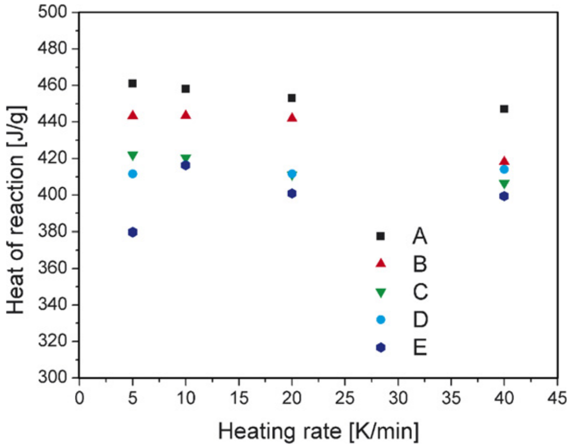

Fig. 3. Total heat of reaction as function of heating rate for epoxy resin systems with different contents of additives and fillers (see Table 1) for nonisothermal curing at different heating rates (between 5 and 40 K/min).

heat of reaction (D). A slightly larger decrease with considerable scatter as a function of heating rate have been found for the resin system containing fillers without surface treatment (E).

The additives introduced seem to act as inhibitors regarding to the reaction between resin and hardener. It is assumed that the additive-molecules interfere with functional groups of the reacting monomers. As a consequence, the final network of the epoxy resin in presence of additives and fillers is not built that homogenously and tightly as that of the pure epoxy resin. This is reflected by a decrease of the total heat of reaction as discussed in respect with the data in Table 2. Both liquid and solid additives may interact with the reacting monomers chemically or physically. To understand this effect in depth, however, further investigations, like IR measurements, are needed.

The difference in total heat of reaction between the resin system with all additives (C) and that one with additionally surface-modified fillers (D) is marginal. However, noticeably lower values of the total heat of reaction can be seen for formulation E which includes nonmodified fillers. To understand the effect of the epoxysilane coated fillers on cure kinetics also the nonmodified fillers need to be considered. In comparison to formulation C the system with all kind of additives and nonmodified fillers (E) shows a lower amount of heat of reaction (reduction up to 35 J/g). Note that the fillers are chemically inert in this case and the stoichiometric ratio between resin and hardener is the same as in formulation C. Therefore the reduction of the total heat of reaction should be traced to the fact that the fillers adsorb the reacting monomers at their surfaces and thus affecting the stochiometry and creating some sterical hindrance in respect to the forming network. On the other hand, surface-modified fillers (formulation D) can be chemically incorporated into the network and thereby contribute to the total heat of reaction. So the appearing higher value of total heat of reaction for the formulation with surface-modified particles (D) compared to the system with nonmodified fillers (E) can be clearly attributed to additional reactions of the epoxysilanes.

Reduction in the heat of reaction was already described in the literature. Hedreul investigated a diglycidyl ether of bisphenol A (DGEBA) curing with amine which showed a total heat of reaction of $440 \pm 20$ J/g. Adding epoxy-terminated liquid nitrile rubber caused a reduction of this value to $300 \pm 25$ J/g [18].

### 4.2. Isothermal curing

From the practical point of view it is important to know the course of conversion with time at isothermal curing conditions. Furthermore the influence of additives and fillers on the cure reaction is of great relevance. So, the nonfilled epoxy resin (A) and the commercial system with all additives and surface-modified fillers (D) were characterized by isothermal DSC-measurements and the outcome compared.

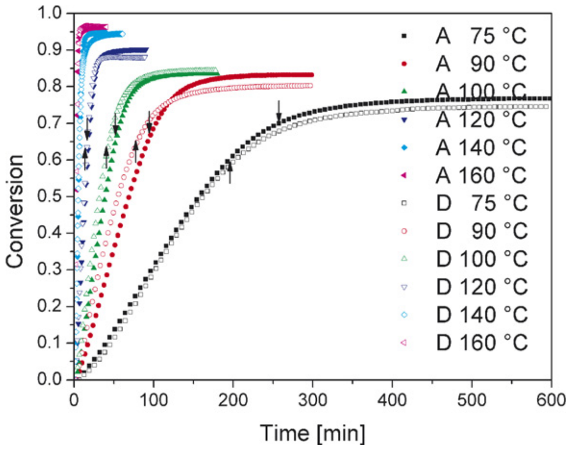

Fig. 4. Conversion as a function of time for the epoxy resin systems (Table 1: formulations A and D) at different temperatures under isothermal hardening. Gel point is marked by arrows.

In Fig. 4 the conversion of the epoxy resin systems A and D is shown as a function of time for different curing temperatures selected between 75 and 160 °C. As expected, for both formulations not only the conversion rate raises with increasing temperature but also the total conversion. In Fig. 4 the gel point derived from rheology measurements (not reported here) is marked with arrows. Gelation occurs when the formation of an infinite network is reached. As filler particles can be incorporated into the network already a lower degree of chemical crosslinks between the particles is sufficient to create a network-like structure in the curing material. As depicted in Fig. 4 the gel conversion of the neat EP resin (A) is about 0.67, whereas its value is between 0.59 and 0.64 for the filled material (D). For both systems (i.e. A and D) the gelling conversion is nearly independent on the curing temperature. Once the vitrification of the resin system is passed the reaction is dominated by diffusion effects. If the cure temperature is too low then the molecular mobility is hindered and thus the final conversion never reaches the unity. This is well resolved on the conversion versus time traces in Fig. 4.

A slight difference between the two investigated systems A and D can be seen. At the beginning of the reaction the filled system (D) shows a marginal higher conversion rate than the nonfilled epoxy resin (A). This is likely due to a slight accelerating effect caused by the fillers and additives. But a higher total conversion was reached for the epoxy resin without fillers (system A). This result is consistent with the lower total heat of reaction of the filled system (D) derived from the nonisothermal DSC scans (Fig. 3). Note that the described effects are very small but in general apparent for almost all measurements.

The basic task when studying the cure kinetics through DSC is to find a mathematical description of the conversion as a function of time and temperature. The equation of Kamal is used to describe the conversion in case of isothermal treatment. Note, that this model description for the conversion as function of time and temperature disregards the exact curing mechanism. Assuming that the order of reaction $n$ and $m = 1$ in Eq. (10) the phenomenological model can be rewritten as

$$\frac{d\alpha}{dt_R}\Big/(1-\alpha) = (k_1 + k_2 \cdot \alpha) \cdot f_d(\alpha) \tag{12}$$

The kinetics of a curing reaction are complex because during curing the viscosity of the system increases and the kinetics, being initially controlled by the chemical reactivity of the functional groups, become controlled by diffusion of these groups. For that reason the diffusion term tends to be zero for small conversions. The plot of $\frac{d\alpha}{dt_R}\Big/(1-\alpha)$ versus conversion results in a straight line with $k_1$ as the intercept and $k_2$ as the slope for conversions where the diffusion can be neglected.

The experimental data of the isothermal DSC-measurements were converted according to the equation of Kamal and plotted as a function of conversion. Four parameters were determined by minimizing the least square error function in order to fit the equation of Kamal to the experimental data: the rate-constants $k_1$, $k_2$, the conversion at the end of reaction $p_{end}$ and the constant of diffusion b. The experimental data of the base resin at 75 and

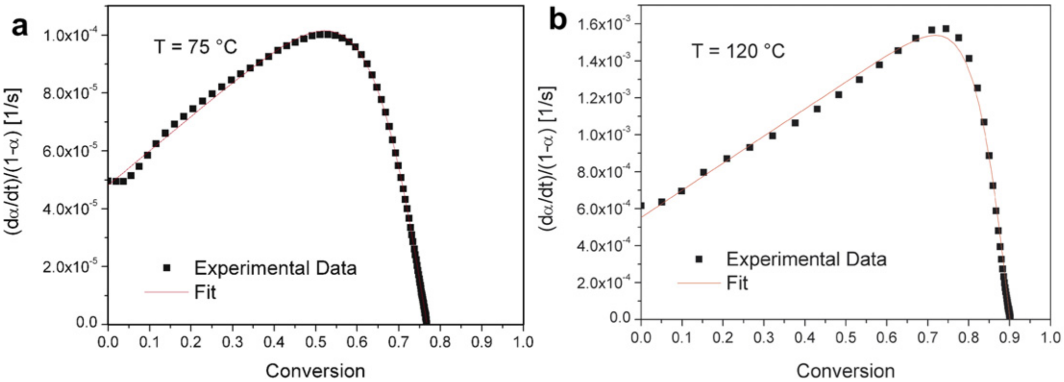

Fig. 5. Plots of $(d\alpha/dt)/(1-\alpha)$ versus conversion for the epoxy resin (Table 1: formulation A) at isothermal curing conditions of 75 (a) and 120 °C (b).

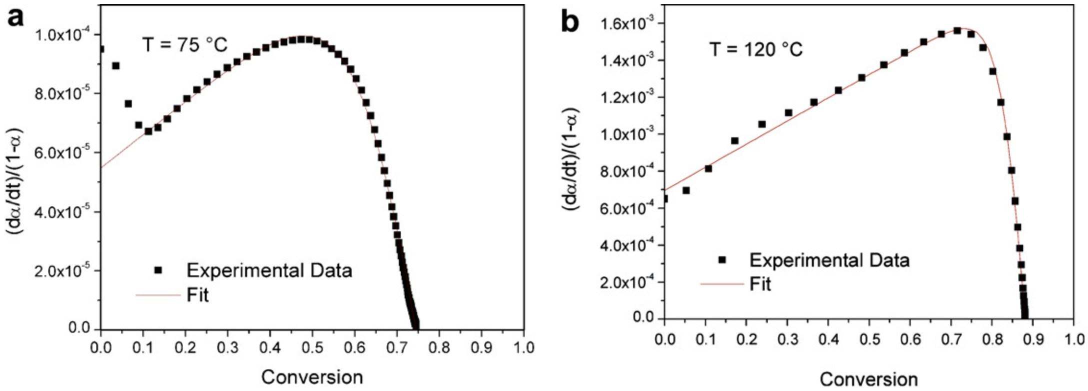

Fig. 6. Plots of $(\mathrm{d}\alpha/\mathrm{d}t)/(1-\alpha)$ versus conversion for the epoxy resin with liquid and solid additives and fillers with modified surface (Table 1: formulation D) at isothermal curing conditions of 75 (a) and 120 °C (b).

120 °C along with the fitted results are displayed in Fig. 5.

After a linear rise up until a conversion of more than 0.5 all curves deviate in the diffusion-controlled region. The curves show a maximum and finally reach a conversion rate of zero at the end of conversion. Note that the fits describe the experimental data very well in the whole conversion range.

The same behaviour is observed for the filled material. Fig. 6 displays similar plots, as shown in Fig. 5, however for the filled material (D). Although additives, fillers and modifiers were incorporated the phenomenological model of Kamal can still well be adopted for the experimental data. The curves shown for 75 and 120 °C, respectively, are characteristic for the temperature range studied (i.e. between 75 and 140 °C). The Kamal model was capable to predict the cure rate versus conversion functions for all isothermal conditions.

In Table 3 the fitting parameters of the modified equation of Kamal for the virgin and filled epoxy systems (Table 1: formulations A and D, respectively) at various curing temperatures are listed. As expected, the calculated conversions at the end of reaction $p_{\mathrm{end}}$ raises with increasing curing temperature. For the diffusion constant $b$ values between 0.02 and 0.07 can be deduced. The obtained reaction rate constants $k_1$ and $k_2$ depend on the temperature and usually obey the Arrhenius law.

$$k_{1/2} = A_{1/2} \cdot \mathrm{e}^{-\frac{E_{1/2}}{RT}} \tag{13}$$

$$\ln k_{1/2} = \ln A_{1/2} - \frac{E_{1/2}}{RT} \tag{14}$$

The results of $k_1$ and $k_2$ are shown in Fig. 7 where $\ln k_{1/2}$ is plotted against the reciprocal curing temperature.

The results show that the autocatalytic kinetic model with $k_1$, $k_2$, $p_{\mathrm{end}}$ and $b$ as variables is useful in providing a phenomenological description of the curing kinetics of the epoxy resin system (A). Even the evolution of conversion of the more complicated, highly-filled epoxy resin that contains more than 50 wt.% inorganic surface-modified fillers and many other additives can be described by the model of Kamal.

Ivankovic investigated a DGEBA/diamine system filled with organically modified montmorillonite. The filler had almost no effect on the cure

Table 3
Fitting parameters of the modified equation of Kamal for the epoxy resin (Table1: formulation A) and the epoxy resin with liquid and solid additives and surface-modified fillers (Table 1: formulation D)

| Curing temperature [°C] | Rate-constant $k_1$ [$\mathrm{s}^{-1}$] | | Rate-constant $k_2$ [$\mathrm{s}^{-1}$] | | Conversion at end of reaction $p_{\mathrm{end}}$ [1] | | Constant of diffusion $b$ [1] | |
|---|---|---|---|---|---|---|---|---|
| Formulation | A | D | A | D | A | D | A | D |
| 75 | 5.0E−5 | 5.0E−5 | 1.2E−4 | 1.1E−4 | 0.7680 | 0.7447 | 0.0773 | 0.0864 |
| 90 | 1.1E−4 | 1.9E−4 | 2.5E−4 | 1.4E−4 | 0.8327 | 0.8020 | 0.0571 | 0.0683 |
| 100 | 2.2E−4 | 2.7E−4 | 4.3E−4 | 4.1E−4 | 0.8374 | 0.8442 | 0.0427 | 0.0549 |
| 120 | 5.5E−4 | 6.9E−4 | 1.6E−3 | 1.3E−3 | 0.9007 | 0.8814 | 0.0505 | 0.0344 |
| 140 | 1.8E−3 | 1.9E−3 | 4.5E−3 | 3.8E−3 | 0.9454 | 0.9465 | 0.0363 | 0.0243 |

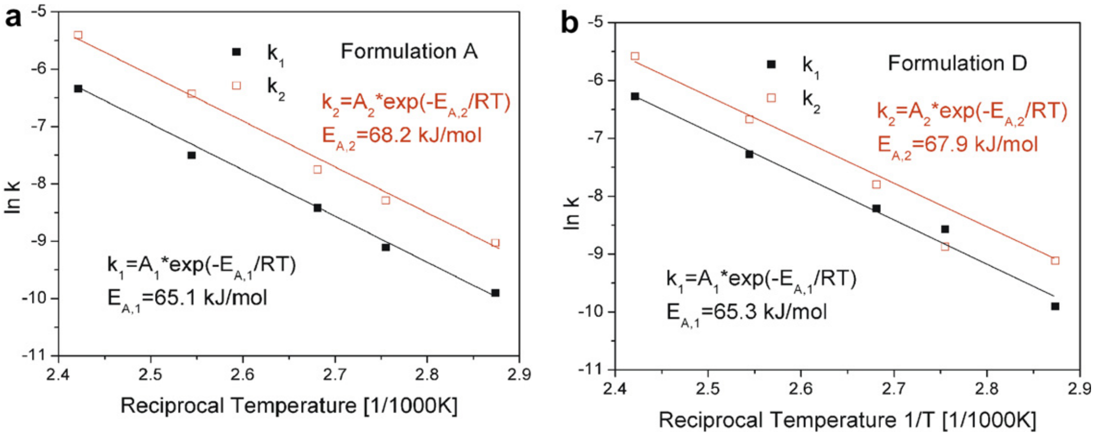

Fig. 7. Plots of ln*k* versus the reciprocal temperature for the epoxy resin systems (Table 1: formulations A (a) and D (b)).

kinetics of the base resin system. In this report the model of Kamal could be fitted to the experimental data only until a conversion of 0.6. It was supposed that at higher conversions the reaction mechanism changes and this is the reason for the deviation from the model [11].

Montserrat showed by temperature modulated DSC measurements that there is a good agreement between the experimental data and those of the model description of Kamal for a DGEBA/anhydride system. Accordingly when the conversion is not reaction-controlled anymore then the temperature modulated technique is not applicable [17].

## 5. Conclusion

The cure kinetics of an anhydride hardened cycloaliphatic epoxy resin with and without additives and fillers were investigated by conventional differential scanning calorimetry (DSC) both under nonisothermal (dynamic) and isothermal conditions. The major conclusions of this study can be summarized as follows:

### 5.1. Dynamic DSC

The additives had an inhibiting effect on the curing according to an increase of the activation energy, whereas $SiO_2$ fillers without surface treatment did not influence the activation energy. Fillers with surface modification showed an accelerating effect on the reaction kinetics of the original epoxy resin as the activation energy was reduced.

Adding any kind of aggregate (liquid and solid additives, modifiers and fillers) to the epoxy resin a reduction of total heat of reaction was observed. Hereby the most significant effect was caused by the additives. Incorporation of surface modified filler had almost no effect on the total heat of reaction, whereas it was reduced for the epoxy system containing the nonmodified $SiO_2$.

### 5.2. Isothermal DSC

The virgin epoxy resin and its version containing additives and surface-modified $SiO_2$ fillers were subjected to isothermal DSC scans. It was found that the conversion of both materials increased with increasing time and temperature. For the filled material, the total conversion was less than the virgin resin. The difference was the larger, lower the cure temperature was. An autocatalytic kinetic model, the Kamal model, extended by a diffusion factor, was applied to the isothermal DSC data. The fitting of the extended Kamal model to the experimental data showed a very good agreement in the whole conversion range for both systems. Therefore the Kamal model with the diffusion term can be used to describe mathematically the curing process of the epoxy systems studied.

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