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The kinetic study of the curing reaction of mono- and di-epoxides obtained during the reaction of divinylbenzene and hydrogen peroxide with acid anhydrides

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Abstract

In this paper, the non-isothermal differential scanning calorimetry (DSC) was employed to investigate the cure process and to determine the kinetic parameters of the curing reactions of mono- and di-epoxides with maleic and glutaric anhydrides. The epoxides were obtained during the epoxidation process of commercially available divinylbenzene by using 60% hydrogen peroxide as the oxidant in the presence of organic solvents and magnesium oxide as the catalyst. It was found that the cure process of epoxides with maleic anhydride was described through higher values of enthalpy of polymerization (ΔH_R) and lower temperatures of the cure initiation (T_{onset}), the peak maximum temperature (T_{max}) and the final cure temperature (T_{end}). It can be considered to accelerate the rate of reaction and lead to an excellent network structure when maleic anhydride was used as curing agent. The kinetic analysis was firstly computed using a model free-estimation of the activation energy (Friedman, Ozawa–Flynn–Wall methods) and then the multivariate non-linear regression with a 6th degree Runge–Kutta process in a modified Marquardt procedure was employed to calculate the corresponding kinetic parameters (E_i, n_i, A_i) using the *n*th-order reaction $f(\alpha)$. The unbranched three-step process of the *n*th-order reaction $f(\alpha)$ for each step was the best to describe the cure process of mono- and di-epoxide with acid anhydrides. The determined values of the activation energies were in the range 64.7–105.2 kJ/mol for epoxides/glutaric anhydride system and 64.7–82.7 kJ/mol when maleic anhydride was used as hardening agent.

Keywords: Epoxides; Differential scanning calorimetry; Cure kinetics

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1. Introduction

The differential scanning calorimetry is one of the conventional experimental techniques in the determination of the heat of reaction, the kinetics and the mechanism of the curing process of different compounds [1,2]. As well known, the epoxides can be cured with a number of nucleophilic and electrophilic reagents. Curing agents such as amines and anhydrides find use in most of the important applications of epoxy compounds and chemical reactions that take place during cure to determine the morphology and properties of the cured materials [3]. The cross-linking reaction with di- or polycarboxylic acid anhydrides is based on the reaction of epoxy groups with anhydride groups to produce ester linkages (hydroxyalkyl esters) via an ionic mechanism. In addition to the ester forming reaction an ether forming reaction is also possible in this system. In the presence of catalytic activation of carboxylic acids at higher temperatures the formation of ether linkages (polyether linkages) is observed [4–9]. The kinetics and mechanism of the curing process of epoxides by acid anhydrides have been extensively investigated. The study of the cure kinetics contributes both a better knowledge of the process development and to improve the quality of the final product [10]. Curing kinetics models are generally developed by analyzing the experimental results obtained by DSC in the

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isothermal and the dynamic modes assuming a proportionality between the heat evolved during the cure and the extent of reaction [11]. In general, kinetics expressions include two kinds of models: phenomenological and mechanistic. The kinetics of the epoxy/anhydride system used to be studied through phenomenological models: the *n*th-order reactions [12] and the auto-catalytic model [13]. Results of the kinetic description of the curing process for different epoxy systems showed that the kinetics of cure may be complicated since it was a multi-step reaction, approaching diffusion controlled region due to vitrification. It was possible to apply the kinetic data for controlling cure conditions, provided that a suitable model has been chosen [14]. The kinetics of the cure reaction of epoxides with acid anhydrides can be described using the *n*th-order reaction $f(\alpha)$. The determined values of the reaction order (n) were ranged from 0.2 to 2 with the values of apparent activation energies from 56 to 159 kJ/mol [15]. The non-isothermal curves of a thermal reaction can satisfy the kinetic equations developed for the kinetic analysis of the *n*th-order reactions, even if they follow a quite different mechanism. Results of the comparative studies lead to the conclusion that the actual mechanism of a thermal process cannot be discriminated from the kinetic analysis of a single DSC trace [16]. Strey et al. [17] have investigated the course of epoxy cure reaction with phthalate anhydride at different heating rates. They have proposed the mechanism of this cure process which was considered as a consecutive reaction (A–B; B–C, where A, B, C represent the hydroxyl groups of the prepolymers (A), the carboxyl groups of the intermediate compounds (B) and the bond between the prepolymers (C) when the concentration of the curing agent was nearly constant during the process.

In the present study, the non-isothermal differential scanning calorimetry was employed to investigate the cure process and to determine the kinetic parameters of the cross-linking reactions of obtained mono- and di-epoxides from commercial grade divinylbenzene. Firstly, the enthalpy of polymerization (ΔH_R), temperatures of the cure initiation (T_{onset}), the peak maximum temperature ($T_{\max}$) and the final cure temperature (T_{end}) of the curing reaction with acid anhydrides were determined. The kinetic analysis was firstly computed using a model free-estimation of activation energy (Friedman, Ozawa–Flynn–Wall methods) and then the multivariate non-linear regression with a 6th degree Runge–Kutta process in a modified Marquardt procedure was employed to calculate the corresponding kinetic parameters (E_i, n_i, A_i) using the *n*th-order reaction $f(\alpha)$.

2. Experimental

2.1. Materials

Commercial grade divinylbenzene (65 wt.% DVB), 35 wt.% ethylvinylbenzene (EVB) stabilized with 4-*tert*-butylpyrocatechol, methanol (99.8 wt.%) and acetonitrile (99.9 wt.%) were obtained from Merck. Aqueous hydrogen peroxide (60 wt.%) was bought from the "Azoty" Nitrogen Plant (Puławy, Poland). Magnesium oxide (MgO) was from POCh (Gliwice, Poland) and was used as an active catalyst. Glutaric anhydride and maleic anhydride were from Aldrich Chemical Company. All chemicals were used without further purification.

2.2. Preparation of epoxides

The epoxidation process [18,19] has been carried out at 50 °C. Magnesium oxide was used as the catalyst in the presence of water adjusted to pH 10 with sodium hydroxide. Commercial grade divinylbenzene (0.192 mol), acetonitrile (1.46 mol), distilled water (50 ml) and magnesium oxide (1.25 g) were charged into the reactor containing condenser, thermometer and stirrer. The reactor was allowed to attain the reaction temperature in a thermostat bath and the mixture of 60% hydrogen peroxide (1.77 mol) and methanol (1.90 mol) was slowly dropped at the reaction temperature while stirring over a period of 2 h. With the 60% hydrogen peroxide the reaction was almost immediately exothermic. The reaction mixture was stirred for a predetermined time (5 h). After completion the liquid product was cooled down to room temperature and the catalyst was separated by filtration. The raw product was washed several times with distilled water. The epoxides were separated from the solvents and by-products by extraction with diethyl ether and dried.

2.3. Technique

All the liquid organic products were identified by GC–MS analysis (GCQ, Thermo-Finnigan, USA). The samples were dissolved in dichloromethane and analyzed using a gas chromatograph with capillary column (Restec RTX-5, 18 m × 18 mm × 0.2 μm; injector PTV 35–300 °C at 10 °C/s) and FID detector at the temperature program 35 °C -1 min/10 °C/min to 300 °C and were analyzed by mass spectrometer with $\mathrm{EI} = 70$ eV and temperature ion volume 220 °C.

The calorimetric measurements were carried out in the Netzsch DSC 204 calorimeter (Günzbung, Germany) operating in a dynamic mode. The non-isothermal scans were performed at different heating rates $\beta = 2$, 5, 10, and 20 K/min from room temperature to a maximum of 300 °C under nitrogen atmosphere (30 ml/min) in order to cure the epoxides and to provide the data for kinetic analysis. The curing process of the obtained epoxides is accomplished using maleic anhydride and glutaric anhydride as curing agents with stoichiometric ratios of anhydrides $r = 0.85$, where r is defined as anhydride groups/epoxy groups. Samples of approximately 10 mg were used in sealed aluminium pans for all experiments. The DSC was previously calibrated using an indium standard. As a reference an empty aluminium crucible was used. All dynamic scans were converted into ASCII files and the kinetic analysis was performed using the Software a Netzsch Thermokinetics Program (Netzsch Gerätebau GmbH, Germany) in the calculation procedure.

3. Results and discussion

3.1. Characterization of epoxides

The characterization of the products (the structure and molecular weight of obtained epoxides) was confirmed by GC–MS analysis. It was found that the epoxidation process of commercial grade divinylbenzene allows to obtain the mixture of epoxides: 45.2% of bis(epoxyethylbenzene), 8.4% of epoxyethylstyrene and 46.4% of 2-ethylphenyloxirane [19].

3.2. Dynamic curing DSC

The obtained mixture of epoxides was cross-linked with glutaric anhydride and maleic anhydride as the hardening agents. The cure behaviours were evaluated using DSC. An exothermic peak is characteristic of the curing reaction. This peak is usually attributed to the epoxy/anhydride copolymerization. The reaction of epoxides with glutaric anhydride (**1**) and maleic anhydride (**2**) is given in Scheme 1.

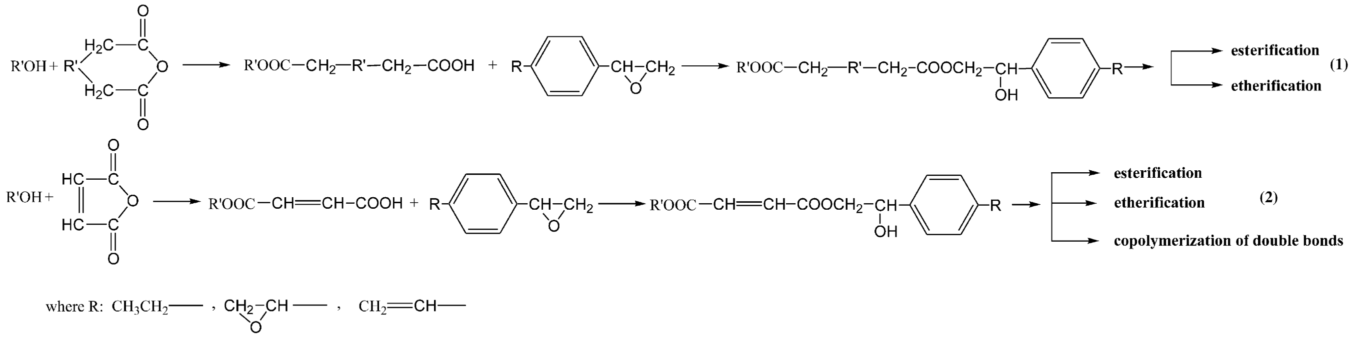
Table 1
DSC data of the curing reaction of the obtained epoxides using glutaric anhydride as the curing agent at different heating rates (β)

β (K/min)	T_{onset} (°C)	T_{max} (°C)	T_{end} (°C)	ΔH_{R} (J/g)
2	44.1	145.3	214.2	457.9
5	53.9	167.3	228.3	473.6
10	88.3	183.7	258.5	483.0
20	91.2	201.0	281.1	496.2

The curing characteristics, such as the temperature of the cure initiation (T_{onset}), the peak maximum temperature (T_{max}), the final cure temperature (T_{end}) and the total heat of the cross-linking reaction (the enthalpy of polymerization process) (ΔH_{R}) obtained as the area [2]:

$$\int_{0}^{t_{\mathrm{c}}} (\mathrm{d}H/\mathrm{d}t)_T \mathrm{d}t,$$

where t_{c} is the curing time and $(\mathrm{d}H/\mathrm{d}t)_T$ is the calorimetric signal during the experimental DSC run. In Tables 1 and 2 were summarized the DSC data of the curing reaction of obtained epoxides using acid anhydrides. Several interesting dependences have been found in the data presented below. Temperature at which the reaction begins, T_{max} and temperature at which the completion of the cure reaction occurs increase with the heating rate β. As it is seen, the maximum of the exotherm peak (T_{max}) and temperatures at which the reaction of the curing process begins and finishes change in dependence of the used hardening agent, too. The maximum peak temperatures are significantly higher for epoxides cured with glutaric anhydride than that for maleic anhydride. The peak maximum temperature for the epoxides/glutaric anhydride system raises from 145.2 °C to 201.0 °C and from 119.5 °C to 167.9 °C for epoxides/maleic anhydride system. Additionally the onset temperature was lower for epoxides/maleic anhydride system in comparison with epoxides/glutaric anhydride system. It is clear that the cure reaction of epoxides/glutaric anhydride system is carried out at relatively high temperature, as reflected in a shift in the exothermic peak from higher and broader temperature range. Use of maleic anhydride as hardening agent should be considered to accelerate the rate of reaction, thus contributing to a decrease in the curing temperature. The sample with maleic anhydride was cross-linked after two days at room temperature. The cross-linking reaction of epoxides/glutaric anhydride has taken more than a week at room temperature. It can be seen that the heat generated during the curing reaction (ΔH_{R}) increases with increasing β. The differences in enthalpies of polymerization have to be attributed to the type of acid anhydrides used. The curing of glutaric anhydride is less exothermic with 447.6 J/g indicating a low conversion for this anhydride. This low heat of reaction is associated with the highest value of the temperature of the exothermic peak maximum (Table 1) indicating a low reactivity probably due to chemical nature of the anhydride. This probably reduces the molecular motions during cure and consequently involves an important amount of non-reacted anhydride in the network [20]. In contrast, the cure reaction of epoxides with maleic anhydride is initiated at relatively low temperature and ΔH_{R} is higher (5168 J/g) than those obtained for epoxides/glutaric anhydride system. Thus, it is expected that this hardening agent can lead to an excellent network structure [21]. This could be attributed to the higher cross-linking density of the cured samples [19]. These results can be explained by the cure mechanism between the epoxides and maleic anhydride. As can be seen from Scheme 1, the curing reaction of the epoxides with acid anhydrides comprises formation of the ester linkages



Scheme 1. The reaction of the obtained epoxides with glutaric anhydride (**1**) and maleic anhydride (**2**).

Table 2
DSC data of the curing reaction of the obtained epoxides using maleic anhydride as the curing agent at different heating rates (β)

β (K/min)	T_{onset} (°C)	$T_{\max}$ (°C)	T_{end} (°C)	ΔH_R (J/g)
2	32.4	119.5	177.8	4982
5	46.5	138.9	190.5	5031
10	63.8	142.8	218.3	5226
20	74.1	167.9	233.7	5433

via an ionic mechanism. Additionally, at higher temperatures, the ether forming reaction is also possible between epoxy groups with secondary hydroxyl groups obtained at first step [9,22–24]. The use of the unsaturated acid anhydride (maleic anhydride) can involve the additional copolymerization reaction of the double bonds and the total heat of reaction increases considerably.

3.3. Kinetic equations and analysis

In general, a kinetic model relates the rate of reaction $d\alpha/dt$ to some function of α and T. It is commonly accepted in the kinetic analysis of the chemical reactions by thermal analysis that any chemical process of reaction will obey a rate law of the form [25,26]:

$$d\alpha/dt = k(T)f(\alpha)$$

where the dependence upon α from the dependence upon T has been separated. Here, t is the time, $f(\alpha)$ is a function of the dependence of conversion (the mathematical expression of the kinetic model) and $k(T)$ is the chemical rate constant which is given by an Arrhenius type equation dependence on the temperature $k = A\exp(-E/RT)$, where A is the frequency factor, E is the activation energy of the reaction, T is temperature in Kelvin and R is the universal gas constant. Using a multiple linear regression, it is possible to determine the kinetic parameters from the DSC exothermal peak obtained from the non-isothermal measurements. In the non-isothermal process the temperature usually increases according to a constant heating $\beta = dT/dt$ ($T = T_0 + \beta t$) [2,27].

In this study the values of apparent activation energy (E) and $\log A$ were firstly determined using a model free-estimation of the activation energy (Friedman, Ozawa–Flynn–Wall methods). These isoconversional methods allow to estimate the activation energy without the need to define a specific model for the reaction run. Friedman proposed the application of the logarithm of the conversion rate $d\alpha/dt$ (with α_t given) as a function of reciprocal temperature:

$$d\alpha/dt = A\exp(-E/RT)f(\alpha)$$

$$\ln(d\alpha/dt) = \ln f(\alpha) + \ln A - (E/RT)$$

As $f(\alpha)$ is a constant for given α_t the plot of dependence $\ln(d\alpha/dt) = f(1/T)$ results in a straight line with the slope $m = -E/R$. From the slope and the intercept of the straight line the value of the activation energy (E) and the logarithm of the pre-exponential factor ($\log A$) can be obtained assuming a first order reaction. The pre-exponential factor is calculated as an average value over all dynamic heating rates β [28,29]. Another isoconversional procedure, introduced by Ozawa–Flynn–Wall, allows to determine the activation energy E (kJ/mol) and the pre-exponential factor A for the nth-order reaction $f(\alpha)$. It is based on the variation of the peak exotherm temperature with the heating rate and the extent of reaction at the peak α is constant and independent of the heating rate. In the Ozawa calculation procedure, the following equation is derived:

$$\ln\beta = \text{const} - 1.052E/RT$$

It can be seen from this equation that for a series of measurements at the heating rates β for a fixed degree of conversion α, the plot of $\ln\beta = f(1/T)$ results in straight lines with a slope $m = -1.052E/R$, where T represents the temperatures at which the conversion α is reached at the heating rate β. The slope of the straight lines is directly proportional to the activation energy. A change in E with an increasing degree of conversion indicates a complex reaction run, so that, in fact, the separation of variables as in OFW analysis is not allowed. These discrepancies are especially serious if the overall reaction is made up of competitive reactions [30,31].

Then the multivariate non-linear regression with a 6th degree Runge–Kutta process in a modified Marquardt procedure was employed to calculate the corresponding kinetic parameters (E_i, n_i, A_i) considering firstly the single reactive process and using the nth-order reaction $f(\alpha)$. Secondly a complex kinetic model considering two- or three-step unbranched reaction process was assumed using the nth-order reaction $f(\alpha)$ in a calculation procedure. The expression of $f(\alpha)$ used in this study is given below:

$$f(\alpha_i) = (1-\alpha_i)^n$$

where n is the order of the reaction [32]. Therefore, the experimental data will be fitting according to the next expression where each reaction is characterized as:

$$d\alpha_i/dt = k_i(T)(1-\alpha_i)^n, \quad i = 1,2,3$$

$$k_i(T) = A_i\exp(-E_i/RT)$$

The obtained average values of the activation energy (E) and the pre-exponential factor (A) for epoxides cross-linked with glutaric and maleic anhydrides computed using isoconversional methods are shown in Table 3. It can be seen that the values obtained by these methods for epoxides cured with glutaric anhydride are slightly higher than those for

Table 3
The activation energy and the pre-exponential factor (A) characteristic of the cured epoxides computed using acid anhydrides applying different kinetic methods

Method	Glutaric anhydride		Maleic anhydride	
	E (kJ/mol)	$\log A$ (s^{-1})	E (kJ/mol)	$\log A$ (s^{-1})
ASTM E698	71.53 ± 3.36	6.13	68.39 ± 2.73	6.29
Friedman	74.03 ± 2.83	6.35	71.23 ± 1.22	6.65
Ozawa–Flynn–Wall	73.57 ± 1.76	6.36	65.82 ± 1.64	6.51

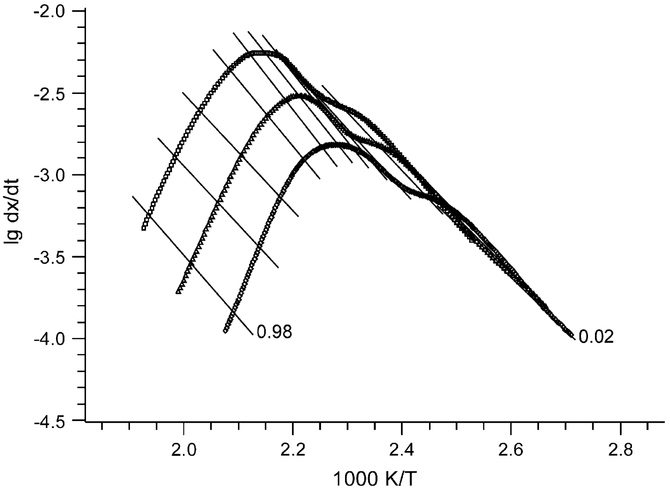


Fig. 1. Friedman analysis of the cure process using glutaric anhydride as a curing agent.

epoxides cross-linked with maleic anhydride. The use of maleic anhydride as the hardener should be considered to accelerate the rate of the reaction, thus contributing to a decrease in the curing temperature and apparent activation energy. Friedman analysis yields information concerning the changeability of E vs. α. As follows from Figs. 1 and 2 the activation energy for epoxide/glutaric anhydride changes with the degree of conversion α. The maxima of E are observed at $\alpha = 0.5$ and 0.7. The presence of maleic anhydride as the hardening agent causes a decrease and relatively stable E and A vs. degree of the conversion profile above $\alpha > 0.2$ and leaving aside $\alpha = 0.6$, where the minimum of E and A was observed (Fig. 3). This leads to conclusion that the changeability of the activation energy with the degree of conversion can be indication of the presence of a complex reaction path (reaction with at least two steps). To test this supposition the one single process using the nth-order reaction $f(\alpha)$ was firstly considered. In the examined range of β 2–20 K/min the received values of activation energy, the $\log A$ and the reaction order (n) were 79.2 kJ/mol, 6.87 and 1.28, respectively, with the coefficient of correlation (r) 0.991 for epoxides/glutaric anhydride system. In the case of epoxides/maleic anhydride system the values of kinetic parameters were $E = 74.8$ kJ/mol, $\log A = 7.17$ and $n = 1.22$ with $r = 0.993$. As can be seen, the calculated apparent activation energy for epoxides/glutaric anhydride system was slowly higher than those obtained when maleic anhydride was used. Additionally, the calculated curves do not fit well with the experimental data (low coefficients of correlation r) so that the one-step model of these reactions does not lead to a satisfactory result and is unable to achieve a good description of the curing reaction of obtained epoxides with acid anhydrides. For further analysis a complex kinetic model has to be applied to describe the course of this reaction. The unbranched reaction process considering two- or three-step reactions of the nth order was found to be the best fit (based on the F-test) with the coefficient of correlation $r > 0.997$ between the simulated curves and the measured data. In the examined range of β the received values of apparent activation energies by considering two-step reaction of the nth order (FnFn) and three-step reaction of the nth order (FnFnFn) are in the range reported by other authors for epoxy/anhydride reactions (Tables 4 and 5) [33]. It was observed

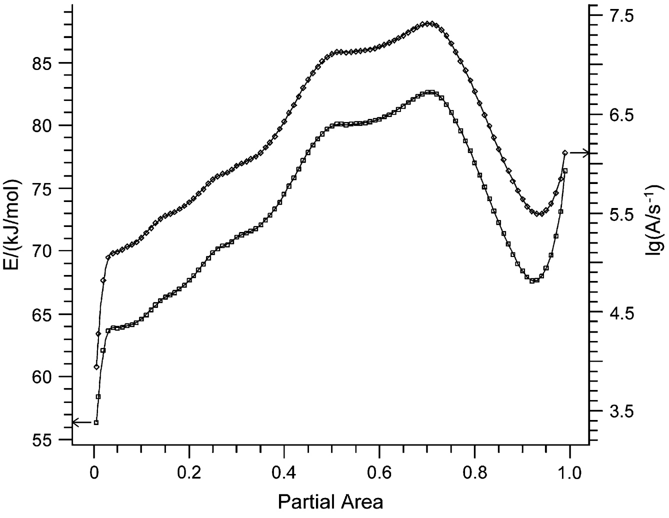


Fig. 2. The activation energy and the pre-exponential factor as a function of degree of the conversion for the cure process of epoxides and glutaric anhydride calculated by Friedman method.

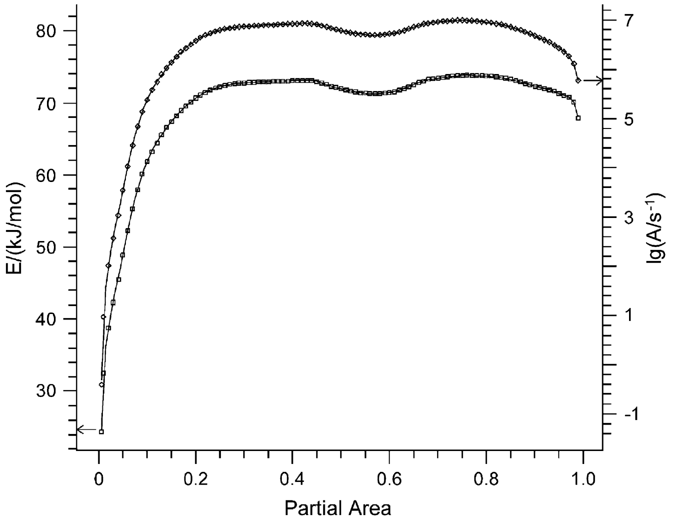


Fig. 3. The activation energy and the pre-exponential factor as a function of degree of the conversion for the cure process of epoxides and maleic anhydride calculated by Friedman method.

Table 4
The kinetic parameters of the experimental data obtained using two-step reaction of the nth order (FnFn)

Parameter	Hardening agent	
	Glutaric anhydride	Maleic anhydride
E_1 (kJ/mol)	61.9	59.9
E_2 (kJ/mol)	96.5	89.6
$\log A_1$ (s^{-1})	5.15	5.75
$\log A_2$ (s^{-1})	9.19	9.16
Reaction order 1 (n_1)	1.27	1.07
Reaction order 2 (n_2)	0.75	1.35
Coefficient of correlation (r)	0.9970	0.9972

Table 5
The kinetic parameters of the experimental data obtained using three-step reaction of the *n*th order (FnFnFn)

Parameter	Hardening agent	
	Glutaric anhydride	Maleic anhydride
E_1 (kJ/mol)	64.7	64.5
E_2 (kJ/mol)	105.2	82.7
E_3 (kJ/mol)	78.6	75.4
$\log A_1$ (s^{-1})	5.40	6.66
$\log A_2$ (s^{-1})	10.0	7.74
$\log A_3$ (s^{-1})	7.62	7.42
Reaction order 1 (n_1)	1.55	1.63
Reaction order 2 (n_2)	1.68	1.02
Reaction order 3 (n_3)	1.85	0.95
Coefficient of correlation (r)	0.9994	0.9980

that the kinetic parameters changed with used curing agent. The system cured with maleic anhydride exhibits lower values of the activation energies than those cross-linked with glutaric anhydride. For the three-step reaction process the activation energies and the reaction orders were $E_1 = 64.5$ kJ/mol, $n_1 = 1.63$, $E_2 = 82.7$ kJ/mol, $n_2 = 1.02$ and $E_3 = 75.4$, $n_3 = 0.95$ when maleic anhydride was used. On the other hand, the values of activation energies for epoxides/glutaric anhydride system were in the range 64.7–105.2 kJ/mol. The successful evaluation (Figs. 4 and 5) indicates sufficient applicability of the used kinetic models for the description of the curing reaction of the obtained epoxides with acid anhydrides. The mechanism of the curing reaction of epoxy compounds with acid anhydrides can be explained as a consecutive process. At first stage, the rate of reaction between the epoxy and the hardener reactive groups is chemically controlled with an initial acceleration due to the presence of compounds with hydroxyl groups, there is no steric hindrance in the surrounding area. The uncatalysed cure can occur through reactions involving monoester, diester and ether linkages forming the real polyepoxide. Then as cure proceeds, the increasing size and complexity of the epoxy oligomers restrict diffusion because the mobility of the reacting groups reduces and the curing process becomes very slow due to vitrification. It seriously affects this process and causes any difficulties in mass transport (diffusion) [33–38].

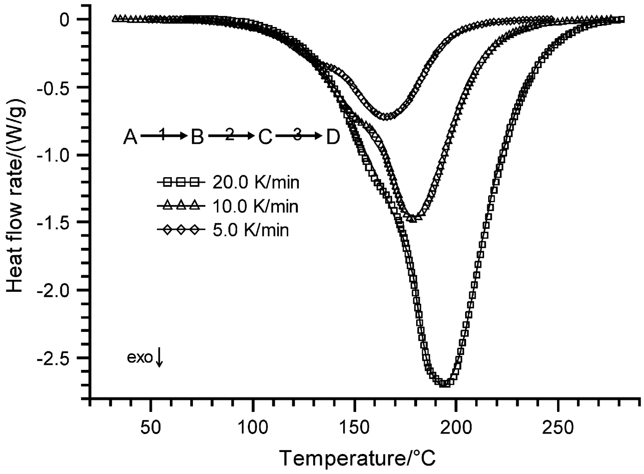


Fig. 4. Experimental DSC curves (full line) and calculated DSC curves (symbols) for the epoxides/glutaric anhydride system considering three-step reaction of the *n*th order at different heating rates.

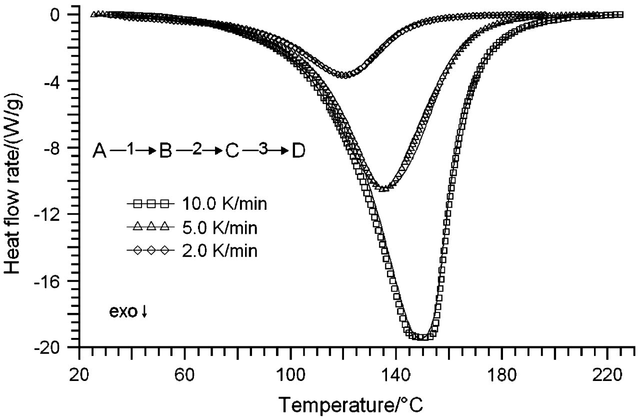


Fig. 5. Experimental DSC curves (full line) and calculated DSC curves (symbols) for the epoxides/maleic anhydride system considering three-step reaction of the *n*th order at different heating rates.

4. Conclusions

The curing process of epoxides obtained during epoxidation of commercially available divinylbenzene by using 60% hydrogen peroxide in the presence of organic solvents and magnesium oxide was examined by DSC. It was found that the cure process of epoxides with maleic anhydride was generally described through higher values of the enthalpy of polymerization (ΔH_R) and lower temperatures of the cure initiation, peak maximum temperature and final cure temperature. This could be attributed to the higher cross-linking density of the epoxides/maleic anhydride system and can lead to better properties of obtained networks due to esterification, etherification and additional copolymerization of the double bonds. The kinetic analysis of the cure process of the obtained epoxides with acid anhydrides was firstly performed using isoconversional methods. The activation energies depend on α indicating a complex reaction path. Then an advanced non-linear regression method by considering one, two-, or three-step unbranched process and using the *n*th-order reaction $f(\alpha)$ had been employed to describe the cure kinetics over the whole range of conversion. The unbranched three-step reaction of the *n*th-order reaction $f(\alpha)$ was found to be the best to describe the cross-linking process of the obtained epoxides with acid anhydrides. As was expected, the system cured with glutaric anhydride exhibited higher activation energies (64.5–105.2 kJ/mol) in comparison with maleic anhydride (64.5–82.7 kJ/mol).

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