Journal of Thermal Analysis and Calorimetry, Vol. 88 (2007) 2, 441–448

STUDY OF POLYMERIZATION KINETICS OF THE UNSATURATED POLYESTER RESIN USINGACETYL ACETONE PEROXIDE AND Co(II)OCTOATE

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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 reaction of the unsaturated polyester resin catalyzed with promoter-cobalt(II)octoate and free-radical initiators. The initiators were formed by the oxidation process of acetylacetone with 60% hydrogen peroxide in the presence of the catalyst-sulphuric acid and the solvents: propano-1,2-diol or the mixture of propano-1,2-diol and hydroxypolyether TG 500. As a reference, the typical curing system containing ethyl methyl ketone hydroperoxide (Luperox) and promoter was used.

It was found that the cure process of the unsaturated polyester resin with the new initiators/cobalt(II)octoate was described through lower maximum peak temperatures (T_{max}) and lower values of the total heat of the curing reaction (ΔH_R) in comparison with Luperox/cobalt(II)octoate. The computed values of activation energies were in the range of 40.8–44.9 and 80.4–87.6 kJ mol^{-1} for unsaturated polyester resin cured with the new initiators/cobalt(II)octoate. The values of activation energies were little lower or comparable to those obtained when Luperox/cobalt(II)octoate system was used (45.8 and 82.3 kJ mol^{-1}).

Keywords: *differential scanning calorimetry, initiators, kinetics of polymerization, organic peroxides*

Introduction

Radical initiation reactions, therefore, can be divided into two general types according to the manner in which the free radical species are formed. These are homolytic decomposition of covalent bonds by energy absorption or electron transfer from ions or atoms containing unpaired electrons followed by bond dissociation in the acceptor molecule [1]. A very effective method of generating free radicals under mild conditions is by one-electron transfer reactions, the most effective of which is redox initiation. This method has found wide application for initiating polymerization reactions and has industrial importance [2, 3]. The most useful types of compounds in generation of radicals at the polymerization temperatures contained fairly specific types of covalent bonds: oxygen-oxygen, oxygen-nitrogen or sulphur-sulphur bonds. Unsaturated polyester resin can be cured at an elevated or at room temperatures. This reaction is a free radical chain-growth copolymerization between the low molecular mass comonomer (i.e. styrene) and the unsaturated vinylene molecules to produce a three-dimensional network structure [4]. To cure the unsaturated polyester resin at room temperature the suitable initiating system is needed. The most commonly source of free radicals are organic peroxides (i.e. ethyl methyl ketone hydroperoxide) [4, 5]. The promoters usually, cobalt or ferrous salts are necessary to obtain the reasonable rates of initiation under ambient temperature conditions because they promote the decomposition of the number of peroxides. The accelerators involve a one-electron transfer from the metal ion to the peroxide with the dissociation of the oxygen-oxygen bond and the generation of the free radicals [6]. The curing reaction is highly exothermal and can be monitored by thermal analysis with differential scanning calorimetry (DSC). This experimental technique allows to determine the heat of the reaction, reaction kinetics and the curing process of different compounds [7–11]. In our previous studies we presented the kinetic study of the curing reaction of the unsaturated polyester resin catalyzed with promoter and the new initiators. We have found that the initiators obtained during the oxidation process of ethyl methyl ketone or cyclohexanone with hydrogen peroxide in the presence of compounds containing hydroxylic groups can be used as an active initiators in the polymerization process of the unsaturated polyester resin. The calculated values of activation energies were in the range of 45.2–50.3 and 89.2–89.8 kJ mol^{-1} for the curing process of unsaturated polyester resin with promoter Co(II) salt and they were comparable to those when the

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1388–6150/$20.00

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Luperox/cobalt(II) salt was used (44.1 and 80.7 kJ mol^{-1} [12, 13]. In the present work, the curing process of unsaturated polyester resin catalyzed with a promoter and the initiators prepared during the oxidation process of acetyl acetone by hydrogen peroxide in the presence of the catalyst and the solvents was investigated kinetically, using DSC in a dynamic mode. The determination of kinetic parameters was firstly carried out using isoconversional methods (Friedman, Ozawa–Flynn–Wall). Then the multivariate non-linear regression-based determination of the reaction function has been used. The corresponding kinetic parameters like activation energy (E), reaction order (n) and the frequency factor (A) were computed considering a single reactive process and using the $\mathrm{n^{th}}$-order reaction $f(\alpha)$ (Fn), $\mathrm{n^{th}}$-order reaction $f(\alpha)$ with autocatalysis (Cn) and first-order reaction $f(\alpha)$ with autocatalysis (C_1), where J_{kat} is the catalyst constant. The functions used are given below by the following expressions, where n is the reaction order [14]:

$$Fn\text{:}\ f(\alpha)=(1-\alpha)^{\mathrm{n}} \tag{1}$$

$$Cn\text{:}\ f(\alpha)=(1-\alpha)^{\mathrm{n}}(1+J_{\mathrm{kat}}^{\alpha}) \tag{2}$$

$$C_1\text{:}\ f(\alpha)=(1-\alpha)(1+J_{\mathrm{kat}}^{\alpha}) \tag{3}$$

As it is known, any chemical process of reaction in the kinetic analysis will obey a rate law of the form [15, 16]:

$$\mathrm{d}\alpha/\mathrm{d}t=k(T)f(\alpha) \tag{4}$$

where $k(T)$ is the chemical rate constant which is given by an Arrhenius type equation dependence on temperature:

$$k(T)=A\ \exp(-E/RT) \tag{5}$$

A is the frequency factor, E-activation energy of the reaction, R the universal gas constant (8.314 J mol^{-1} K^{-1}) and T-temperature in Kelvin [7, 17]. Therefore, the experimental data was fit according to the next three expressions:

$$\mathrm{d}\alpha/\mathrm{d}t=\mathrm{Ae}(-E/RT)(1-\alpha)^{\mathrm{n}} \tag{6}$$

$$\mathrm{d}\alpha/\mathrm{d}t=\mathrm{Ae}(-E/RT)(1-\alpha)^{\mathrm{n}}(1+J_{\mathrm{kat}}^{\alpha}) \tag{7}$$

$$\mathrm{d}\alpha/\mathrm{d}t=\mathrm{Ae}(-E/RT)(1-\alpha)(1+J_{\mathrm{kat}}^{\alpha}) \tag{8}$$

Then, for further analysis a complex kinetic model was applied to describe the course of the curing reaction. The unbranched reaction process considering two-step reactions of $\mathrm{n^{th}}$-order function $f(\alpha)$ for each step was assumed in a calculation procedure.

Experimental

Materials

The unsaturated polyester resin A023 was kindly obtained from the Chemical Plant 'Erg' (Pustków, Poland). Acetyl acetone and sulphuric acid were delivered by POCh (Gliwice, Poland). Propano-1,2-diol and hydroxypolyether TG 500 (prepared from glycerin and propylene oxide with the average molecular mass 560 g mol^{-1} and functionalities 3) were from the Chemical Plant 'Rokita' (Brzeg Dolny, Poland). Hydrogen peroxide (60%) was bought from the 'Azoty' Nitrogen Works (Puławy, Poland). Luperox (50% solution of ethyl methyl ketone hydroperoxide in dimethyl phthalate) was from the 'Luperox' (Günzburg, Germany). Cobalt(II) octoate–1% solution in styrene was from POCh (Gliwice, Poland).

Preparation of the initiators

Hydrogen peroxide (60%) was dropped into the reactor containing acetyl acetone, sulphuric acid as the catalyst and the solvents: propano-1,2-diol or the mixture of propano-1,2-diol and hydroxypolyether TG 500 while stirring. The addition of hydrogen peroxide was made at such a rate that the temperature of the mixture content was 35°C. The homogeneous solution after the addition of the whole amount of hydrogen peroxide was stirred for 2 h. One week after the synthesis, the raw product was analyzed by DSC and GC-MS methods and used as an initiator for free radical polymerization of the unsaturated polyester resin A023 with promoter–1% solution of cobalt(II)octoate. In this way two new liquid initiators were prepared (Fig. 1). The amounts of the substrates used for their syntheses are shown in Table 1.

Methods

Characterization of the initiators

The concentrations of an active oxygen in all initiators were determined by titration of an initiator sample

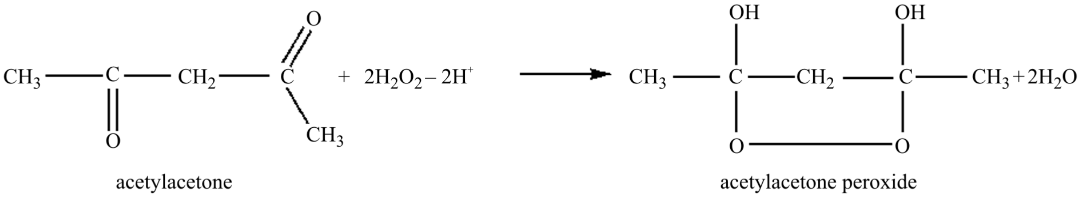

Fig. 1 Examplary synthesis of hydroperoxide compound

Table 1 The chemical composition of the obtained initiators

Initiator No.	Substrates/g			
	Hydrogen peroxide	Acetyl acetone	Propano-1, 2-diol	TG 500
1	60	26	20	20
2	60	53	100	–

Table 2 The concentration of an active oxygen in the studied initiators

Initiator No.	Oxygen/%	
	calculated	measured
1	13.3	13.1
2	7.9	7.8

(dissolved in acetic acid) by 0.1 N solution of sodium thiosulphate in the presence of potassium iodine and starch according to Królikowski *et al.* [18]. The concentrations of an active oxygen in the studied initiators are given in Table 2.

All the initiators were identified by GC-MS analysis (GCQ ,Thermo-Finnigan, USA). The samples were dissolved in dichloromethane and quantified using a gas chromatograph with capillary column (Restec RTX-5, 18 m·18 mm·0.2 μm; injector PTV 35–300°C 10°C s^{-1}) and FID detector at the temperature program from 35 to 300°C with a heating rate 10°C min^{-1} and were analysed by mass spectrometer with EI=70eV and temperature ion volume 220°C.

The calorimetric measurements of the new initiators and Luperox were made to evaluate decomposition temperatures (T_d) and the heat of the decomposition (ΔH_d). The DSC analysis was performed on the differential scanning calorimeter Netzsch DSC 204 (Netzsch, Germany). The samples were heated from room temperature to approximately 450°C with the heating rate of 10 K min^{-1} in aluminium crucibles and under nitrogen atmosphere.

DSC measurements

The obtained initiators and Luperox (50% solution of ethyl methyl ketone hydroperoxide in dimethyl phthalate) were used for cross-linking the commercially available unsaturated polyester resin A023. The calorimetric measurements were carried out in Netzsch DSC 204 calorimeter (Netzsch, Germany). All DSC measurements were done in aluminum pans with a pierced lid. A standard sample was prepared by mixing 10 g of unsaturated polyester resin with a fixed proportion of initiator and promoter (100:1:0.1) for approximately 1 min. The required amount of the sample (20 mg) was weighted into previously weighted sample pan, sealed and placed in the DSC for each measurement. After each run, the mass of the sample was determined again to check any mass loss due to evaporation of styrene monomer. No significant mass loss was observed. The dynamic scans were performed from –10 to 250°C using a nitrogen atmosphere and different heating rates β 2–50 K min^{-1}. All dynamic scans were analyzed with using the Software a Netzsch Thermokinetics Program (Netzsch Gerätebau GmbH, Germany) in the calculation procedure.

Kinetic analysis

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 applies 6-th degree Runge-Kuta process in a modified Marquardt procedure was employed to calculate the corresponding kinetic parameters (E_i, A_i, n_i) using the the n^{th}-order reaction $f(\alpha)$ (Fn), n^{th}-order reaction $f(\alpha)$ with autocatalysis (Cn) and first–order reaction $f(\alpha)$ with autocatalysis (C_1).

Results and discussion

It was found that the oxidation process of acetyl acetone in the presence of the catalyst-sulphuric acid allow to obtain the hydroperoxide compound with the molecular mass of 134 g mol^{-1} (acetyl acetone peroxide) and retention time of 11.52 min (Fig. 2). The used solvent propano-1,2-diol and unreacted acetyl acetone were observed at retention times 3.93 and 4.51 min, respectively. In the case of Luperox the mixture of hydroperoxide compounds with the molecular mass 210 g mol^{-1} (ethyl methyl ketone hydroperoxide) and 106 g mol^{-1} (ethyl methyl peroxide) with the retention time 11.72 and 9.46 min were observed (Fig. 3). Ethyl methyl ketone and the solvent – dimethyl phthalate were identified at retention times 5.35 and 19.18 min.

From the DSC curves of the new initiators (Nos 1, 2) the endothermic and exothermic peaks were observed (Fig. 4). The first (endothermic) peak at 115.1 or 125.8°C was probably due to the evaporation of unreacted substrates and the used solvents. The second exothermic peak was expected to be the decomposition of an organic peroxide-acetyl acetone peroxide. The decomposition of the Luperox was characterized by two signals. The first, exothermic at 157°C was described the decomposition of ethyl methyl ketone hydroperoxide and the second was exhibited the evaporation of the dimethyl phthalate (at 255.7°C). The heat of the decomposition (ΔH_d) of the new initiators estimated from the area under the DSC curve and decomposition temperatures (T_d) are given in Table 3.

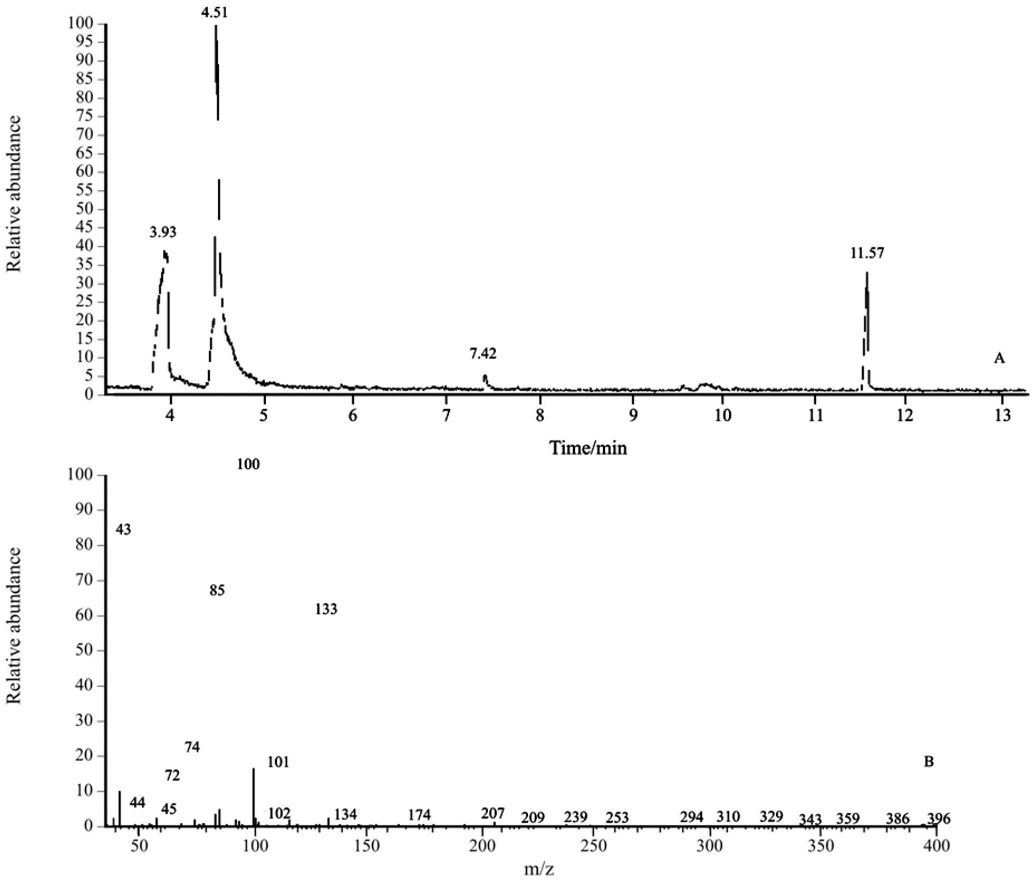

Fig. 2 A – GC chromatogram and B – MS spectrum of the initiator No. 2

Table 3 The heat of the decomposition (ΔH_d) and decomposition temperatures (T_d) of the initiators

Initiator No.	T_1/°C	ΔH_{d1}/Jg^{-1}	T_2/°C	ΔH_{d2}/Jg^{-1}
1	125.8	549.7	151.9	340.7
2	115.1	423.7	154.3	456.6

The new initiators were characterized by higher ΔH_d values during decomposition in comparison with the standard initiator-Luperox (ΔH_d=233.5 kJ mol^{-1}).

The cure behaviors of the unsaturated polyester resin with the redox system: Co(II)octoate/initiators were evaluated using DSC. The DSC curves showed an asymmetrical exothermic peak, which could be due to two different reactions taking place in the unsaturated polyester resin [19]. The heat of the cross-linking reaction (ΔH_R) estimated from the area under DSC curve and the maximum peak temperature (T_{max}) are given in Table 4. Several interesting dependences have been found on the data presented in Table 4. The temperature at which the reaction begins and the exothermic peak temperature increase with β. The temperature at which the completion of the cure reaction occurs increases with β, too. The maximum peak temperatures were significantly higher for the resin cross-linked with redox system: Luperox-Co(II)octoate than for new initiators-Co(II)octoate. The peak maximum temperature for unsaturated polyester resin polymerized with typical system: Luperox-Co(II) octoate raised from 63.8 to 146.6°C. On the other hand the resin cured with the new initiators-Co(II) octoate exhibited the lower temperatures from 56.4 to 118.9°C for initiator No. 1 and from 61.2 to 126.8°C for initiator No. 2.

The heat of reaction is due to a cross-linking reaction between the polyester double bonds and the styrene double bonds. However, the organic peroxide decomposition is a highly exothermal reaction and different free-radical initiator systems can give different values for ΔH_R [8, 11, 17, 20, 21]. It can be seen that the heat generated during the curing reaction decreases with the increasing β from 10 to 50 K min^{-1}. In the case of the resin polymerized in the presence of the new initiators (Nos 1 and 2) and cobalt(II)octoate slightly lower values of heat generated during the reaction are observed in comparison with the typical redox system: Luperox–cobalt(II)octoate. The average values of 336.0 J g^{-1} for Luperox, 321.9 J g^{-1} for initiator No. 1 and 279.8 J g^{-1} for initiator No. 2 were assigned to the heat of polymerization of the unsaturated polyester resin. Other investigators have

Table 4 Total heat of the reaction ΔH_R and the exothermic peak temperature T_{max} at different heating rates for unsaturated polyester resin

β/K min^{-1}	Luperox		Initiator No. 1		Initiator No. 2	
	T_{max}/°C	ΔH_R/J g^{-1}	T_{max}/°C	ΔH_R/J g^{-1}	T_{max}/°C	ΔH_R/J g^{-1}
2	63.8	291.3	56.4	372.8	61.2	366.2
5	80.9	351.4	70.3	360.5	77.2	346.8
10	85.4	375.7	79.9	394.1	88.5	300.9
15	91.1	372.3	88.7	375.9	97.3	277.9
20	115.4	362.7	89.1	274.9	101.2	258.3
30	124.3	304.9	102.7	237.8	112.5	211.7
50	146.6	293.8	118.9	237.6	126.8	196.8

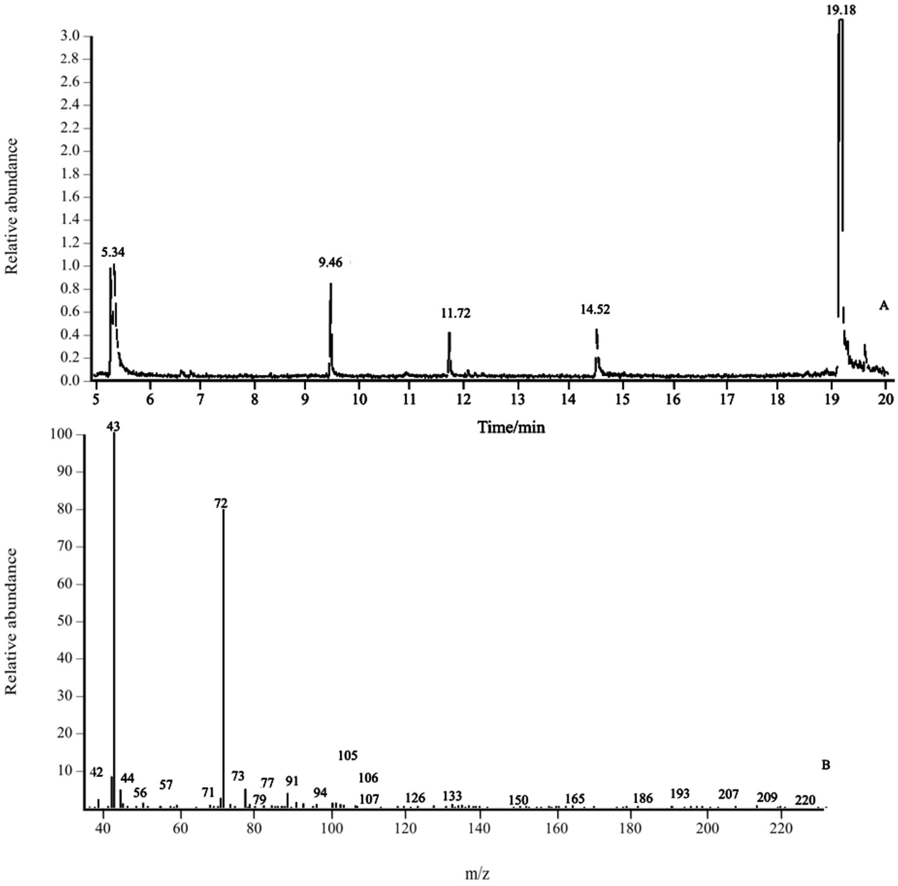

Fig. 3 A – GC chromatogram and B – MS spectrum of the Luperox

reported a range of heat of polymerization from 292.6 to 426 J g^{-1} for the unsaturated polyester resins. This range may be due to different types of unsaturated polyester resin and free-radical initiator systems employed [19, 22–24].

Model-free estimation of activation energy

In this study the values of activation energy (*E*) and pre-exponential factor (*A*) were firstly determined using a model free-estimation of activation energy (ASTM E698-79, Friedman, Ozawa–Flynn–Wall methods). These isoconversional methods allow to estimate of the activation energy without the need to define a specific model for the function run. Within the kinetic analysis, the model-free estimation of the activation energy is used as a powerful preliminary stage to solve the inverse reaction kinetics of complex reactions. The numerous kinetic method using the variation of peak exotherm with the heating rate such as well-established ASTM E698-79 treats the complex cure as a single-step reaction of first order.

The activation energy evaluated by this method is a single point on the dependence of E on α at $\alpha=\alpha_{max}$ [25]. Friedman proposed the application of the logarithm of the conversion rate $d\alpha/dt$ (with α_t given) as a function of reciprocal temperature:

$$d\alpha/dt=A\exp(-E/RT)f(\alpha) \qquad (9)$$

$$\ln(d\alpha/dt)=\ln f(\alpha)+\ln A-(E/RT) \qquad (10)$$

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 ($\lg A$) can be obtained. The pre-exponential factor is calculated as an average value over all dynamic heating rates β [26, 27]. Another isoconversional procedure, introduced by Ozawa–Flynn–Wall, allows to determine the activation energy E (kJ mol^{-1}) and pre-exponential factor A whatever the mechanism. It is based on the variation of peak exotherm temperature with heating rate and the extent of reaction at the peak α is constant and independent of heating rate. In the Ozawa calculation procedure, the following equation is derived:

$$\ln\beta=\text{const}-1.052E/RT \qquad (11)$$

It can be seen from this equation that for a series of measurements at 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 of $m=-1.052\ E/R$ 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 of 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 [28, 29].

It can be seen that the values obtained by ASTM E698-79 method for unsaturated polyester resin cured with the new initiators Nos 1 and 2 and a promoter Co(II)octoate are slightly higher than those for resin polymerized with the catalytic system: Luperox-Co(II)octoate. The activation energy (E) and the pre-exponential factor ($\lg A$) obtained using the ASTM E698-79 analysis for the unsaturated polyester resin cured with catalytic system: Luperox-Co(II)octoate were 41.8 kJ $mol^{-1}\pm1.02$ and 3.92, respectively. Use of new initiators as hardeners caused little increase the E and $\lg A$, the values of activation energy and the pre-exponential factors were 42.0 kJ $mol^{-1}\pm1.32$ and 3.95 for initiator No. 1 and 46.33 kJ $mol^{-1}\pm1.66$ and 4.29 for initiator No. 2. Friedman analysis yields information concerning the changeability of E *vs.* α (Figs 5, 6). As follows from Tables 5, 6 and 7 the activation energy for all used catalytic systems: initators-cobalt(II)octoate changed with the degree of conversion α. In the case of the resin polymerized with the catalytic system: Luperox-cobalt(II)octoate, the minimal value of the E was observed at $\alpha=0.3$, whereas for the curing system: initiator No.1-cobalt(II)octoate and initiator No.2-cobalt(II)octoate the minima of E are observed at $\alpha=0.6$ and $\alpha=0.7$, respectively. This leads to conclusion that the changeability of the activation energy with the degree of conversion can be indicated the presence of a complex reaction path (reaction with

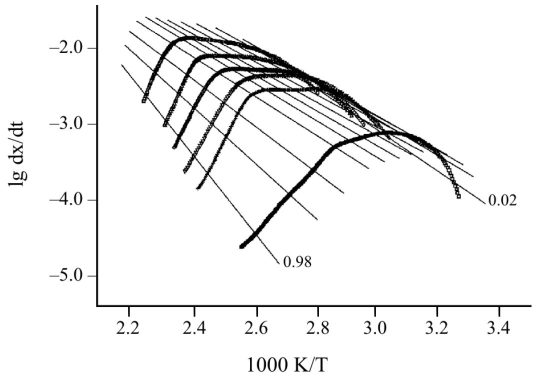

Fig. 5 Friedman analysis of the cure process of the resin with catalytic system: Luperox–cobalt(II)octoate

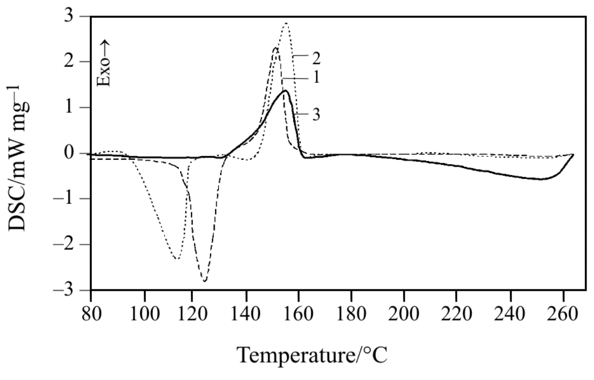

Fig. 4 DSC curves of the initiators: Luperox (3); initiator No. 1 (1); initiator No. 2 (2)

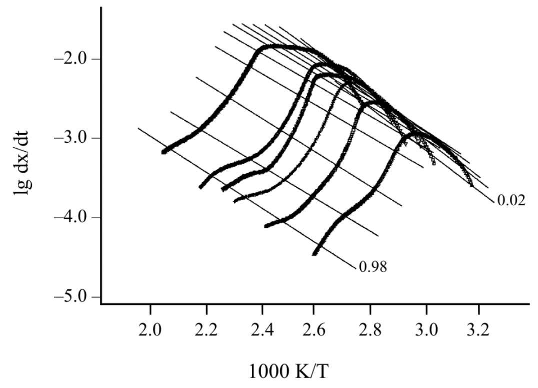

Fig. 6 Friedman analysis of the cure process of the resin with catalytic system: initiator No. 2–cobalt(II)octoate

Table 5 The values of activation energy E (kJ mol^{-1}) and the logarithm of the pre-exponential factor (lg$A$) obtained by Friedman's method for resin curing with catalytic system containing Luperox and cobalt(II)octoate

α	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	0.95	0.99
E/kJ mol^{-1}	44.00 ±0.70	42.14 ±1.23	41.22 ±1.51	41.22 ±1.64	42.26 ±1.79	44.37 ±1.80	46.44 ±1.79	48.75 ±1.90	58.02 ±3.12	69.76 ±2.89	89.94 ±2.88
lg$A$/s^{-1}	4.05	3.80	3.66	3.64	3.78	4.10	4.36	4.69	5.85	7.26	10.43

Table 6 The values of activation energy E (kJ mol^{-1}) and the logarithm of the pre-exponential factor (lg$A$) obtained by Friedman's method for resin curing with catalytic system containing Initiator No. 1 and cobalt(II)octoate

α	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	0.95	0.99
E/kJ mol^{-1}	44.66 ±3.91	46.42 ±3.73	42.50 ±2.46	38.83 ±1.63	36.98 ±1.47	36.09 ±1.58	36.99 ±2.01	37.64 ±2.53	40.96 ±3.11	40.38 ±2.85	59.06 ±2.99
lg$A$/s^{-1}	4.10	4.42	3.80	3.35	3.22	3.18	3.23	3.26	3.71	3.65	5.70

Table 7 The values of activation energy E (kJ mol^{-1}) and the logarithm of the pre-exponential factor (lg$A$) obtained by Friedman's method for resin curing with catalytic system containing Initiator No. 2 and cobalt(II)octoate

α	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	0.95	0.99
E/kJ mol^{-1}	50.91 ±1.09	47.27 ±1.79	43.36 ±2.38	41.02 ±2.69	39.75 ±2.83	39.06 ±2.81	37.99 ±2.90	38.14 ±3.35	41.19 ±3.03	39.32 ±2.08	47.05 ±2.86
lg$A$/s^{-1}	5.06	4.60	4.06	3.75	3.59	3.51	3.36	3.31	3.43	2.89	3.71

Table 8 Kinetic parameters of experimental data obtained with two-step reaction of nth-order functions $f(\alpha)$ (FnFn) for unsaturated polyester resin cured with a catalytic system: initiator–cobalt(II)octoate

Catalytic system	Kinetic parameters							
	logA_1	E_1/kJ mol^{-1}	n_1	logA_2	E_2/kJ mol^{-1}	n_2	Fexp	r
Luperox-Co(II)octoate	4.18	45.8	0.95	7.87	82.3	1.61	1.00	0.9981
Initiator No. 1-Co(II)octoate	3.68	40.8	1.05	7.66	80.4	1.19	1.00	0.9982
Initiator No. 2-Co(II)octoate	4.10	44.9	1.07	8.32	87.6	1.28	1.00	0.9985

at least two steps). The average values of E and lg$A$ obtained using the Ozawa–Flynn–Wall analysis for the resin cured with the catalytic system: Luperox-cobalt(II)octoate were 44.79 kJ mol^{-1}±1.23 and 4.03. In the case of the resin polymerized with the redox system: new initiators-cobalt(II)octoate, the following values of the activation energies and the lg$A$ were obtained: 40.39 kJ mol^{-1}±1.72 and lg$A$=3.95 for the redox system: initiator No.1-cobalt(II)octoate and 47.26 kJ mol^{-1}±1.61 and lg$A$=4.41 for the resin cured with initiator No. 2-cobalt(II)octoate.

Multivariate non-linear regression

In the examined range of heating rate (β) 2–50 K min^{-1}, the activation energy (E) varies insignificantly with the change of the type of used reaction model. The one single reactive process using the nth-order reaction $f(\alpha)$ (*Fn*), nth-order reaction $f(\alpha)$ with autocatalysis (*Cn*) and first-order reaction $f(\alpha)$ with autocatalysis (C_1) had been employed. Comparisons of different kinetic models leads to the conclusion that reaction of nth-order with autocatalysis (*Cn*) is the best statistical fit on the basis of the F-test procedure. The received values of E, lg$A$ and n were 49.2 kJ mol^{-1}, 4.22 and 0.98 with the coefficient of correlation r 0.987 for the resin cured with catalytic system: Luperox-Co(II)octoate. In the case of resin polymerized with new initiators-cobalt(II)octoate the calculated values of E, lg$A$ and n were 41.2 kJ mol^{-1}, 3.87 and 1.05 for initiator No. 1 and 47.6 kJ mol^{-1}, 4.12 and 1.10 for initiator No. 2 with the coefficient of correlation 0.991 for others. As can be seen (the low coefficient of correlation) the one step model does not lead to satisfactory results and was unable to achieve a good description of the curing reaction of the unsaturated polyester resin with the redox system: cobalt(II)octoate/initiators. For further analysis a complex kinetic model was applied to describe the course of the curing reaction. The unbranched reaction process considering two-step reaction of nth-order was found to be the best (based on F-test) with coefficient of correlation above 0.998 between the simulated curves and measured data. In the examined range 2–50 K min^{-1}, the activation energies of the cure process of unsaturated polyester resin with the catalytic system: Luperox-cobalt(II)octoate were 45.8 and 82.3 kJ mol^{-1}. In the case of catalytic system: new initiators-cobalt(II)octoate the calculated activation energies of the cure process of the resin were lower than those obtained for catalytic system: Luperox-cobalt(II)octoate. Additionally, the system cured with initiator No. 2-cobalt(II)octoate exhibited higher values of activation energies than those cross-linked with initiator No. 1-cobalt(II)octoate. This may be due to the fact that the initiator No. 1 was richer in free radicals than others, free radicals could be evolved by both hydrogen peroxide and acetyl acetone peroxide formed by the oxidation of acetyl acetone with hydrogen peroxide in the presence of sulphuric acid as the catalyst. The values of activation energies for the resin cross-linked with initiator No. 1-Co(II)octoate were 40.8 and 80.4 kJ mol^{-1}. The use of catalytic system: initiator No. 2-Co(II)octoate allowed to obtain the following values of E: 44.9 and 87.6 kJ mol^{-1} (Table 8). The successful evaluation (r values) indicated sufficient applicability of the used kinetic model for the description of curing reaction of unsaturated polyester resin with promoter and new initiators obtained during the oxidation process of acetyl acetone with hydrogen peroxide in the presence of the catalyst and compounds containing hydroxylic groups.

Conclusions

The curing process of commercially available unsaturated polyester resin with the redox system: promoter and new initiators obtained during the oxidation of acetyl acetone by hydrogen peroxide in the presence of the catalyst and solvents was investigated by DSC. Luperox-promoter system was used as a reference. It was found that the cure process was described through lower peak maximum temperatures and lower values of ΔH_R when the redox system: new initiators and cobalt(II)octoate was used. The values of kinetic parameters were firstly determined by model-free isoconversional methods. The activation energies were depending on α indicating a complex kinetic scheme. The proposed unbranched reaction process for the resin polymerized with the redox system: initiator-promoter considering two steps and using n$^{\text{th}}$-order function $f(\alpha)$ better described the polymerization process (r above 0.998) than one single process. The calculated values of activation energies were in the range 40.8–44.9 and 80.4–87.6 kJ mol^{-1} for the curing process using cobalt(II)octoate-new initiators and 45.8 and 82.3kJ mol^{-1} when the redox system: Luperox-cobalt(II)octoate was used. The activation energies for each process were in accordance with tabulated values for typical free-radical polymerizations initiated by the redox decomposition of the initiator at low temperatures and by the thermal decomposition of the initiator at high temperatures [8, 12, 30].

References

1 A. S. Sarac, Prog. Polym. Sci., 24 (1999) 1149.
2 G. C. Misra and V. D. N. Bajpai, Prog. Polym. Sci., 8 (1982) 61.
3 G. C. Misra, Encyclopedia Polym. Sci., 8 (1985–1989) 61.
4 H. Yang and L. J. Lee, J. Appl. Polym. Sci., 79 (2001) 1230.
5 J. M. Salla, A. Cadenato, X. Ramis and J. M. Morancho, J. Therm. Anal. Cal., 56 (1999) 771.
6 H. H. G. Jellinek, Pure Appl. Chem., 4 (1962) 419.
7 A. A. Duswalt, Thermochim. Acta, 8 (1974) 57.
8 J. L. Martin, Polymer, 40 (1999) 3451.
9 J. M. Salla and J. L. Martin, J. Thermal Anal., 42 (1994) 1025.
10 J. Grenet, S. Marais, M. T. Legras, P. Chevalier and J. M. Saiter, J. Therm. Anal. Cal., 61 (2000) 719.
11 J. M. Filipovic, D. M. Petrovic-Dakov, Lj. P. Vrhovec and J. S. Velickovic, J. Thermal Anal., 38 (1992) 709.
12 M. Worzakowska, J. Appl. Polym. Sci., 102 (2006) 1870.
13 T. Matynia and M. Worzakowska, European Conference on Calorimetry and Thermal Analysis for Environment, 2005, Zakopane, proceedings pages 159–165.
14 J. Šesták, Thermophysical Properties of Solids, their Measurements and Theoretical Thermal Analysis, Elsevier, Amsterdam 1984.
15 B. Dickens and J. H. Flynn, in C1D Crawer (Ed.) Polymer Characterization ACS 2003, Washington 1983.
16 J. Šesták, Thermophysical Properties of Solids Comprehensive Analytical Chemistry, Vol. 13, Elsevier, Amsterdam Chap. 12., 1984.
17 J. L. Martin, A. Cadenato and J. M. Salla, Thermochim. Acta, 306 (1997) 115.
18 W. Królikowski, Z. Kłosowska-Wołkowicz and P. Penczek, Żywice i Laminaty Poliestrowe, WNT, Warsaw 1986, p. 240.
19 E. L. Rodriguez, Polym. Eng. Sci., 31 (1991) 1022.
20 F. Severini and R. Gallo, J. Thermal Anal., 30 (1985) 841.
21 J. Escribano, R. Masegosa, D. Nava, M. G. Prolongo and C. Salom, J. Therm. Anal. Cal., 86 (2006) 675.
22 T. R. Cuadrato, J. Borrado, R. J. Williams and F. M. Clana, J. Appl. Polym. Sci., 28 (1983) 485.
23 H. Ng and I. Mana-Zloczower, Polym. Eng. Sci., 29 (1989) 1097.
24 M. Avella, E. Martuscelli and M. Mazzola, J. Thermal Anal., 30 (1985) 1359.
25 ASTM E698-79, Standard test method for Arrhenius kinetic constants for thermally unstable materials, ASTM, Philadelphia, 1979.
26 H. L. Friedman, J. Polym. Lett., 4 (1966) 323.
27 H. L. Friedman, J. Polym. Sci., 6 (1965) 183.
28 T. Ozawa, Bull. Chem. Soc. Jpn., 38 (1965) 1881.
29 J. Flynn and A. Wall, Polym. Lett., 4 (1966) 232.
30 G. Odian, Principles of Polymerization 3rd Ed., Wiley, New York 1991.

DOI: 10.1007/s10973-006-8055-7