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Application of isoconversional and multivariate non-linear regression methods for evaluation of the degradation mechanism and kinetic parameters of an epoxy resin

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ABSTRACT

The thermo-oxidative degradation of an epoxy resin obtained by curing of an industrially produced DGEBA mixture with 4,4′-methylene-dianiline (MDA) and used as electric insulator has been investigated by TG + DTG + DSC simultaneous analyses performed in static air atmosphere, at five heating rates. TG, DTG and DSC curves showed that, in the temperature range 25–900 °C, a glass transition followed by three thermo-oxidative processes occur. The processing of the non-isothermal data corresponding to the first process of thermo-oxidation was performed by using Netzsch Thermokinetics – A Software Module for Kinetic Analysis. The dependence of the activation energy, evaluated by isoconversional methods, on the conversion degree and the relative high standard deviations of this quantity show that the investigated process is a complex one. The mechanism and the corresponding kinetic parameters were determined by multivariate non-linear regression program and checked for quasi-isothermal data. It was pointed out that the first process of thermo-oxidation of the investigated resin consists in four steps, each step having a specific kinetic triplet. The obtained results were used for prediction of the thermal lifetime of the material corresponding to some temperatures of use and the end point criterion 5% and 10% mass loss.

1. Introduction

The remarkable properties of epoxy resin derived materials (mechanical and electrical properties, chemical resistance, etc.) determine their wide use in the polymer industry like adhesives, coating, moulding, composites, electrical insulating materials, encapsulates for semiconductors. The practical use of these materials requires the knowledge of their thermal stability that is valuable in it and is used to predict the useful life, which involves the investigation of the isothermal and non-isothermal degradation of these materials at relatively high temperatures in inert or oxidative atmospheres. According to the procedure recommended by IEC-216 Standard [1], in order to predict the thermal lifetime, the polymeric material is subjected to isothermal accelerated aging by following the changes in time of a property of interest (mechanical property, electrical property, mass loss). In the kinetic analysis of the results of experiments performed for thermal lifetime prediction, it is assumed that the investigated material exhibits a predominant elementary process of degradation. This procedure requires 8–10 months of gathering experimental data for a given material and a given property. A more rapid procedure is suggested by IEC-1026 Standard [2], according to which the activation energy of the predominant degradation process is evaluated from data obtained using some analytical techniques (gas chromatography, mass spectrometry, isothermal differential calorimetry). This Standard does not recommend using the rapid non-isothermal techniques, such TG, DTA and DSC, since these methods require extrapolation of test results over a large temperature span. However, the results reported by some investigators [3–13] show that a careful kinetic analysis of the non-isothermal data leads to the values of the activation energy that can be used for rapid prediction of the thermal lifetime of the polymeric materials characterized by a single process of degradation. A more difficult problem is the prediction of the thermal lifetime for materials that exhibit complex mechanisms of degradation involving several elementary steps (consecutive, parallel and/or opposed reactions) characterized by the corresponding set of kinetic triplets (activation energy, pre-exponential factor, conversion function). In such cases the non-isothermal data obtained by thermal analysis techniques could be used to give a reasonably accurate description of the kinetics of degradation. The following software packages, available only for commercial use, were elaborated for kinetic analysis of non-isothermal data

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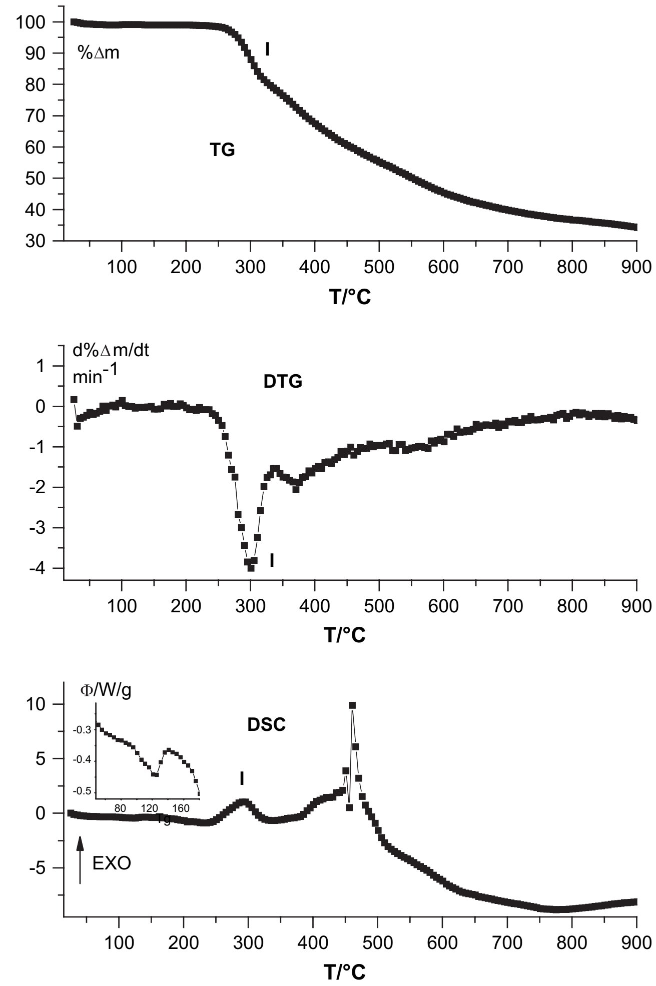

Fig. 1. TG, DTG and DSC curves for the investigated epoxy resin heated in static air, at a heating rate of 10.11 K min^{-1}.

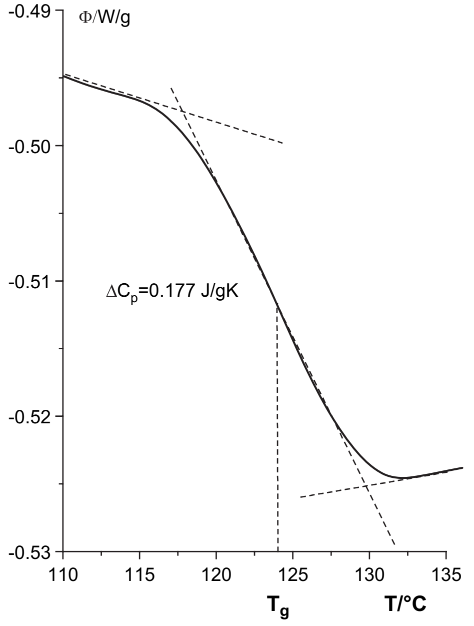

Fig. 2. DSC curve corresponding to glass transition, obtained using DSC 204 F1 Phoenix apparatus.

corresponding to single step and multi-step processes: TA-KIN for Windows v1.6 (Anderson et al. [14]); NETZSCH Thermokinetics (Opfermann [15]); KINETICS for Windows 95/98/NT (Burnham and Braun [16]); AKTS for Windows 95–98 (Roduit [17,18]). Each of these numerical techniques uses the isoconversional and model fitting methods associated with some statistical criteria in order to provide the kinetic scheme (one-step, multi-step) and the corresponding kinetic triplet. The computations should be carried out with experimental data obtained from at least three different heating rates because the model fitting methods that use single heating rate tend to produce highly ambiguous kinetic description (see the conclusions of the ICTAC Kinetic Project [19]).

In some recent work [20–31] thermal analysis methods (TG, DTG, DTA, DSC, DMA) were used for investigation of the thermal and/or thermo-oxidative stabilities of some sorts of resins or composite materials based on epoxy resins. The main processes that occur on the progressive heating of each material were shown and for some of them the non-isothermal kinetic parameters were evaluated. For some of the materials investigated [21,23,28,30,31], the analysis of TG, DTG, DSC or DTA curves shows that the degradation exhibits complex mechanisms. One has to notice that, for a given complex process, the validity of the mechanism and corresponding kinetic parameters was not checked by the comparison the calculated and experimental isotherms.

The aim of this paper has been the investigation of the thermo-oxidative destruction of an epoxy resin, obtained by curing of

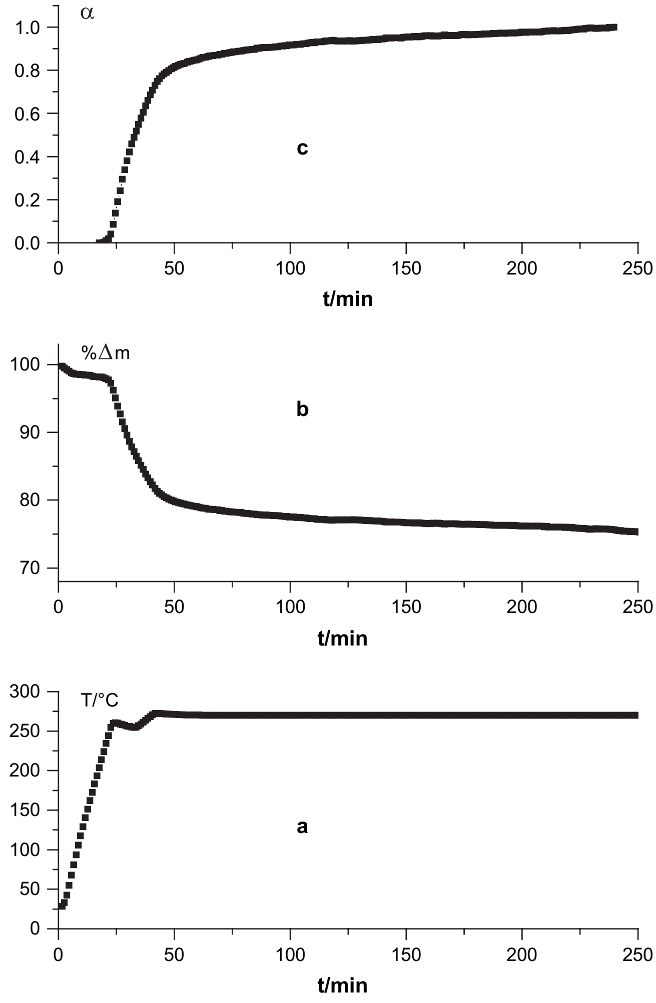

Fig. 3. Temperature program (a), TG curve (b) and conversion degree vs. time curve (c) for the quasi-isothermal experiment.

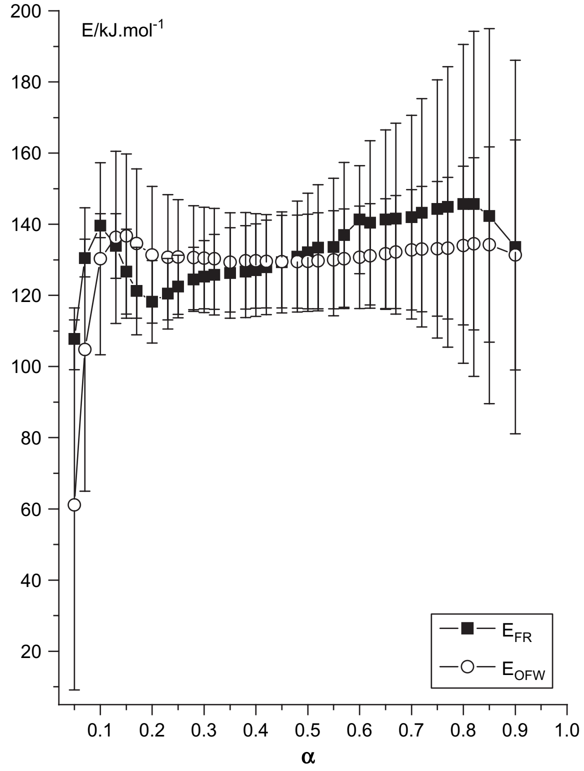

Fig. 4. Dependence of the activation energy evaluated by means of isoconversional methods on the conversion degree, for process I of thermo-oxidation of the epoxy resin.

a DGEBA industrially produced mixture with 4,4′-methylene-dianiline (MDA), by simultaneous TG + DTG + DSC analysis, and the use of TG data for the evaluation of the kinetic parameters of the first process of oxidation shown in thermal curves recorded at several heating rates.

2. Experimental

2.1. Materials

The investigated epoxy resin was synthesized by heating at 70 °C for 20 min of a mixture of the resin 010S (a mixture of DGEBA $n = 0$ and DGEBA $n = 1$ in the ratio of ≈90:10), produced by POLICOLOR – Bucharest – Romania, and 4,4′-methylene-dianiline (MDA), produced by Bayer-Leverkusen – Germany. The ratio of resin 010S:MDA was 91:9. The obtained material has a relatively high electric strength (≈15 kV mm^{-1}) and therefore is used as electric insulator.

Table 1
F-test on fit-quality

Nr.	Code	F_{exp}	F_{crit} (0.95)	*f*-act	Type 1	Type 2	Type 3	Type 4
0	q:f,f,c	1.00	1.47	75	An	An	An	Fn
1	q:f,f,f	1.09	1.48	69	An	Fn	An	Fn
2	q:f,f,f	1.14	1.49	68	Fn	Fn	Fn	Fn
3	t:f,f	1.81	1.49	68	An	An	An	
4	t:f,f	1.82	1.49	68	An	Fn	An	
5	t:f,f	1.83	1.49	68	Fn	Fn	Fn	
6	d:f	1.84	1.48	70	An	Fn		
7	t:f,f	1.89	1.49	67	An	Fn	Fn	
8	s:	2.38	1.48	72	Fn			
9	s:	3.53	1.48	72	An			

2.2. Thermal analysis

The heating curves (TG, DTG and DSC) of the epoxy resin were simultaneously recorded with STA 490C apparatus produced by Netzsch – Germany, in static air atmosphere, in the temperature range 25–900 °C, at the following heating rates: 4.95 K min^{-1}, 7.50 K min^{-1}, 10.11 K min^{-1}, 12.83 K min^{-1} and 15.55 K min^{-1}, and using Pt–Rh crucible. The sample mass was in the range 7.0–7.2 mg.

In order to check the non-isothermal kinetic parameters and the corresponding mechanism, the thermal analysis of epoxy resin was also performed in static air atmosphere and the following temperature program (quasi-isothermal program for $T = 270$ °C):

$$33\,^{\circ}\mathrm{C} \xrightarrow{11.1\ \mathrm{K\,min^{-1}}} 254.5\,^{\circ}\mathrm{C} \xrightarrow{3.05\ \mathrm{K\,min^{-1}}} 260.6\,^{\circ}\mathrm{C} \xrightarrow{-0.8\ \mathrm{K\,min^{-1}}}$$

$$254.5\,^{\circ}\mathrm{C} \xrightarrow{2.1\ \mathrm{K\,min^{-1}}} 272.2\,^{\circ}\mathrm{C} \xrightarrow{-0.1\ \mathrm{K\,min^{-1}}} 270\,^{\circ}\mathrm{C} \overset{272\ \mathrm{min}}{\rightarrow} 270\,^{\circ}\mathrm{C}$$

For a more exact evaluation of the glass transition temperature, the DSC curve of the resin was also recorded using DSC 204 F1 Phoenix apparatus produced by Netzsch – Germany, in the following conditions: temperature range 25–150 °C; synthetic air (purity 99.999%) flow (20 ml min^{-1}); heating rate 10 K min^{-1}; aluminium crucible. The sample mass was 5.3 mg.

2.3. Processing of the experimental data

"Netzsch Thermokinetics – A Software Module for the Kinetic Analysis of Thermal Measurements" was used for processing of

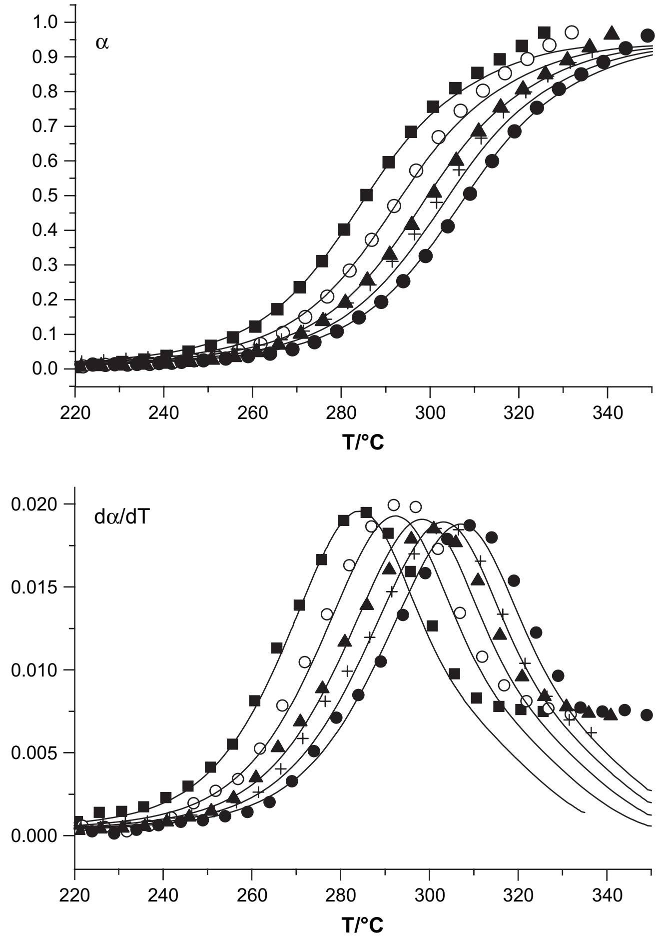

Fig. 5. Fit of the measurements through four step method q:f,f,c with the conversion functions An–An–An–Fn. Experimental: ■: 4.95 K min^{-1}; ○: 7.50 K min^{-1}; ▲: 10.11 K min^{-1}; +: 12.83 K min^{-1}; ●: 15.55 K min^{-1}. Calculated: —.

non-isothermal data. The basic concepts of this Program have been given in Ref. [15]. Recently [31–39], this program was used for the kinetic analysis of some non-isothermal data recorded at several heating rates.

The isoconversional differential method suggested by Friedman [40] (FR method) and the isoconversional integral method suggested independently by Ozawa [41], and by Flynn and Wall [42] (OFW method) were applied for evaluation of the dependence of the activation energy on the conversion degree.

"Multivariate non-linear regression" program was applied for the determination of the complex mechanism of the investigated process and the kinetic parameters characteristic for each reaction step.

3. Results and discussions

Fig. 1 shows the simultaneous TG, DTG and DSC curves obtained for the investigated resin, recorded at 10.11 K min^{-1}; similar curves were obtained for all heating rates. The DSC curve obtained by using the more sensitive DSC 204 F1 Phoenix apparatus is presented in Fig. 2. According to these thermograms, the following processes occur at the progressive heating of the resin: a glass transition characterized by $T_g = 124\,°C$ and $\Delta C_p = 0.177\ J\,g^{-1}\,K^{-1}$; and three (at least) global processes with the formation of volatile compounds. In the temperature range 25–220 °C the sample mass is constant and no exothermic or endothermic peaks were observed

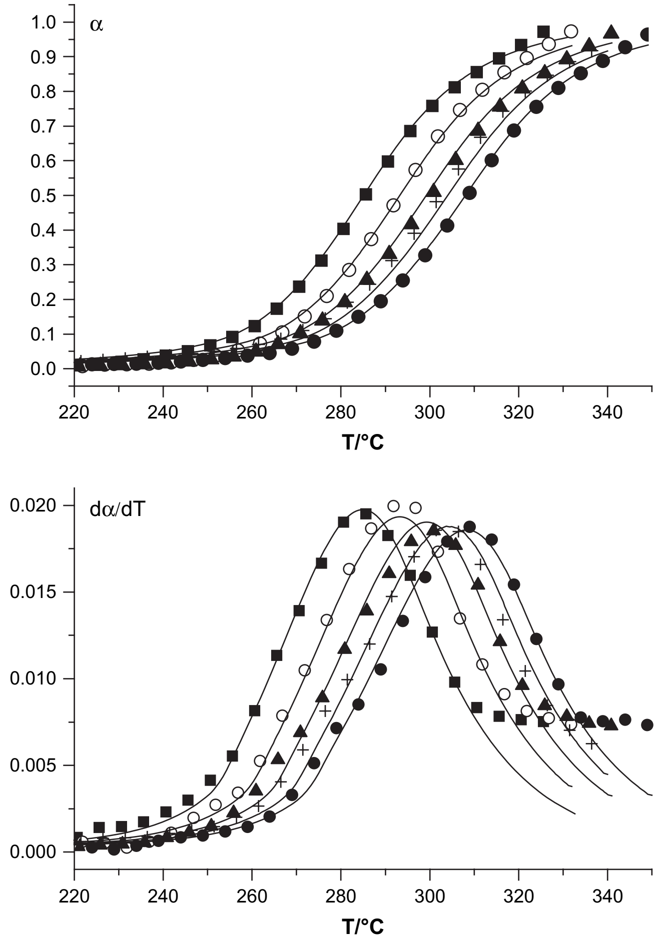

Fig. 6. Fit of the measurements through four step method q:f,f,f with the conversion functions An–Fn–An–Fn. Experimental: ■: 4.95 K min^{-1}; ○: 7.50 K min^{-1}; ▲: 710.11 K min^{-1}; +: 12.83 K min^{-1}; ● 15.55 K min^{-1}. Calculated: —.

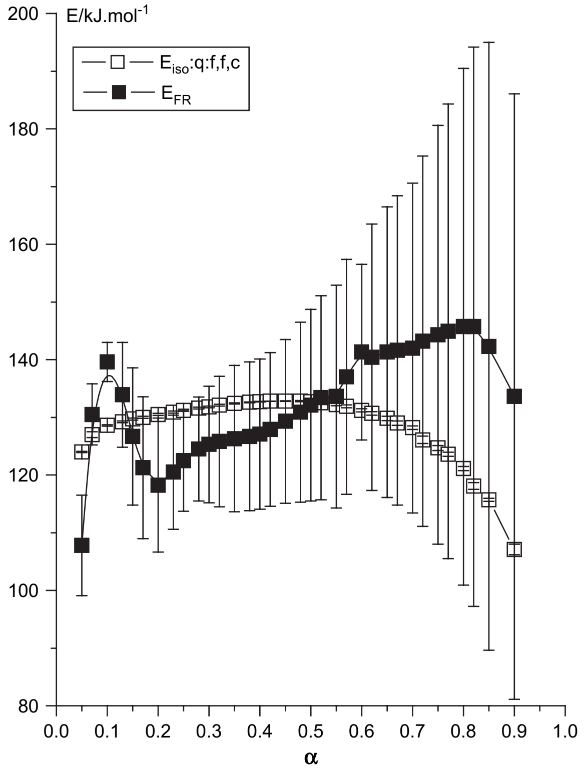

Fig. 7. Comparison between the values of E obtained by differential isoconversional method from experimental non-isothermal data (E_{FR}) and isothermal data calculated using the kinetic parameters corresponding to q:f,f,c scheme (E_{iso}; $T = 170$–$250\,°C$, with a step of 10 °C).

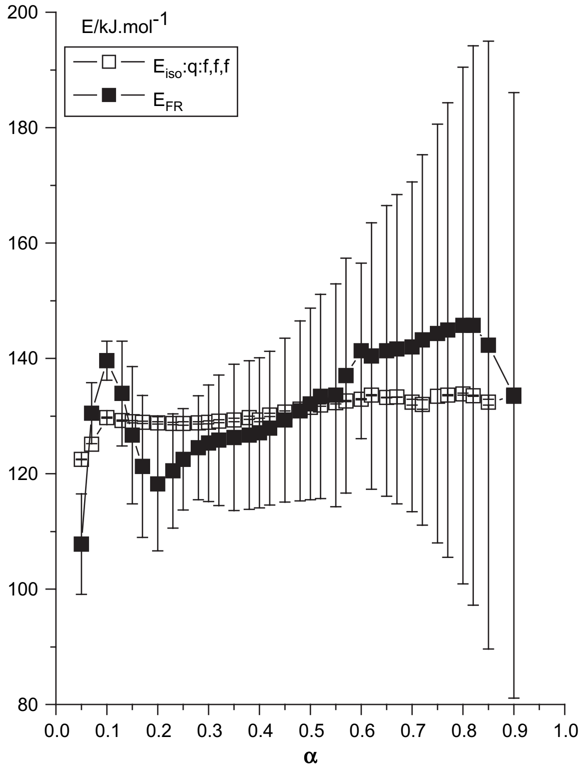

Fig. 8. Comparison between the values of E obtained by differential isoconversional method from experimental non-isothermal data (E_{FR}) and isothermal data calculated using the kinetic parameters corresponding to q:f,f,f scheme (E_{iso}; $T = 170$–$250\,°C$, with a step of 10 °C).

in the DSC curve. The high values of electrical strength and glass transition temperature denote a high cure degree, whose value cannot be evaluated from our thermal analysis data. For the practical use of this material, we are interested in the evaluation of its thermo-oxidative stability.

The kinetic analysis was performed for the first exothermic process of thermo-oxidation, denoted by I in Fig. 1, characterized by a mass loss of 21.8 ± 1.3%. The suitability of such determination is supported by the good reproducibility of thermal analysis results. Some thermal analyses performed in identical conditions show that the relative standard deviations of mass losses and temperatures are lower than 5% and 0.5%, respectively. On the other hand, for different heating rates, the mass losses corresponding to each process are in good agreement (for the heating rates of 4.95 $\mathrm{K\,min^{-1}}$, 7.50 $\mathrm{K\,min^{-1}}$, 10.11 $\mathrm{K\,min^{-1}}$, 12.83 $\mathrm{K\,min^{-1}}$ and 15.55 $\mathrm{K\,min^{-1}}$ the mass losses are: in process I, 20.1%, 19.0%, 20.4%, 21.2% and 21.9%; in the second process of thermo-oxidation, 23.0%, 23.4%, 24.9%, 23.9% and 21.6%).

The results obtained in quasi-isothermal experiment ($T = 270\,^{\circ}\mathrm{C}$) are shown in Fig. 3. According to TG curves from Figs. 1 and 3, only the first thermo-oxidation process occurs in the conditions of a quasi-isothermal experiment.

It is difficult to establish how much of the observed mass loss in process I is due to incomplete cure. Our aim is the evaluation of the kinetic parameters of this thermo-oxidative process because the mass loss by thermal aging of an epoxy resin can be correlated with the changes of its electric properties [1,3,4].

3.1. Model-free estimation of the activation energy according to Friedman and Ozawa–Flynn–Wall methods

The results obtained by application of FR and OFW methods are presented in Fig. 4. Both E_{FR} and E_{OFW} exhibit values of the relative standard deviation higher than 10% and depend on the conversion degree (especially in the range $0.05 \le \alpha \le 0.20$, α is the conversion degree). The differences between E_{FR} and E_{OFW} values were explained [43,44] by the relations that ground the isoconversional methods. In the following we will refer to results obtained by FR method that uses the point values of the overall process rate and unlike OFW method does not include by integration the history of the system in the range 0–α.

3.2. Modelling as multiple-step reaction

The dependence of E on α and the high values of standard deviations for the activation energy evaluated by isoconversional methods show that process I of thermo-oxidation of the investigated resin is complex. In order to find the mechanism of this process and the corresponding kinetic parameters, we used the "Netzsch Thermokinetics" program. The non-isothermal data recorded at the above mentioned five heating rates were brought together during analysis and the relevant differential equations of the reaction rates were numerically solved and the kinetic parameters were iteratively optimized. The calculations were performed in the range of the conversion degree $0.05 \le \alpha \le 0.95$ and considering the following conversion functions:

- reaction order model, Fn: $f(\alpha) = (1-\alpha)^n$ (n is the reaction order);
- Avrami–Erofeev model, An: $f(\alpha) = n(1-\alpha)[-\ln(1-\alpha)]^{(1-1/n)}$ (n is a constant parameter).

The following schemes (mechanisms) of process I were also taken into account:

- scheme coded by s: A → B
- scheme coded by d:f: A – 1 → B – 2 → C
- scheme coded by t:f,f: A – 1 → B – 2 → C – 3 → D
- scheme coded by q:f,f,f: A – 1 → B – 2 → C – 3 → D – 4 → E
- scheme coded by q:f,f,c: A – 1 → B – 2 → C – 3 → D;

C – 4 → E

(the codifications are those used in "Netzsch Thermokinetics" program; A, B, C, D and E are solid compounds; 1, 2, 3, 4 denote the mechanism steps).

Table 2
Non-isothermal kinetic and statistic parameters after non-linear regression through the most two probable mechanisms of the first thermo-oxidation process of the investigated resin

q:f,f,c with the kinetic models An–Fn–An–Fn		q:f,f,f with the kinetic models An–An–An–Fn	
Parameter	Value	Parameter	Value
$\log A_1/\mathrm{s^{-1}}$	8.282	$\log A_1/\mathrm{s^{-1}}$	8.259
$E_1/\mathrm{kJ\,mol^{-1}}$	107.0	$E_1/\mathrm{kJ\,mol^{-1}}$	107.0
n_1	0.630	n_1	0.455
$\log A_2/\mathrm{s^{-1}}$	10.291	$\log A_2/\mathrm{s^{-1}}$	10.259
$E_2/\mathrm{kJ\,mol^{-1}}$	133.0	$E_2/\mathrm{kJ\,mol^{-1}}$	133.0
n_2	1.180	n_2	1.827
$\log A_3/\mathrm{s^{-1}}$	11.311	$\log A_3/\mathrm{s^{-1}}$	12.342
$E_3/\mathrm{kJ\,mol^{-1}}$	150.0	$E_3/\mathrm{kJ\,mol^{-1}}$	138.0
n_3	0.712	n_3	4.000
$\log A_4/\mathrm{s^{-1}}$	6.843	$\log A_4/\mathrm{s^{-1}}$	12.660
$E_4/\mathrm{kJ\,mol^{-1}}$	120.0	$E_4/\mathrm{kJ\,mol^{-1}}$	120.0
n_4	2.000	n_4	2.000
FollReact 1	0.07	FollReact 1	0.07
FollReact 2	0.50	FollReact 2	0.60
ComptReact 3	0.80	FollReact 3	0.10
ComptReact 4	21.30		

Statistic parameters			Statistic parameters		
Correlation coefficient	Durbin–Watson factor	t-Critical (0.95; 69)	Correlation coefficient	Durbin–Watson factor	t-Critical (0.95; 69)
0.998701	2.754	1.987	0.998700	2.970	1.986

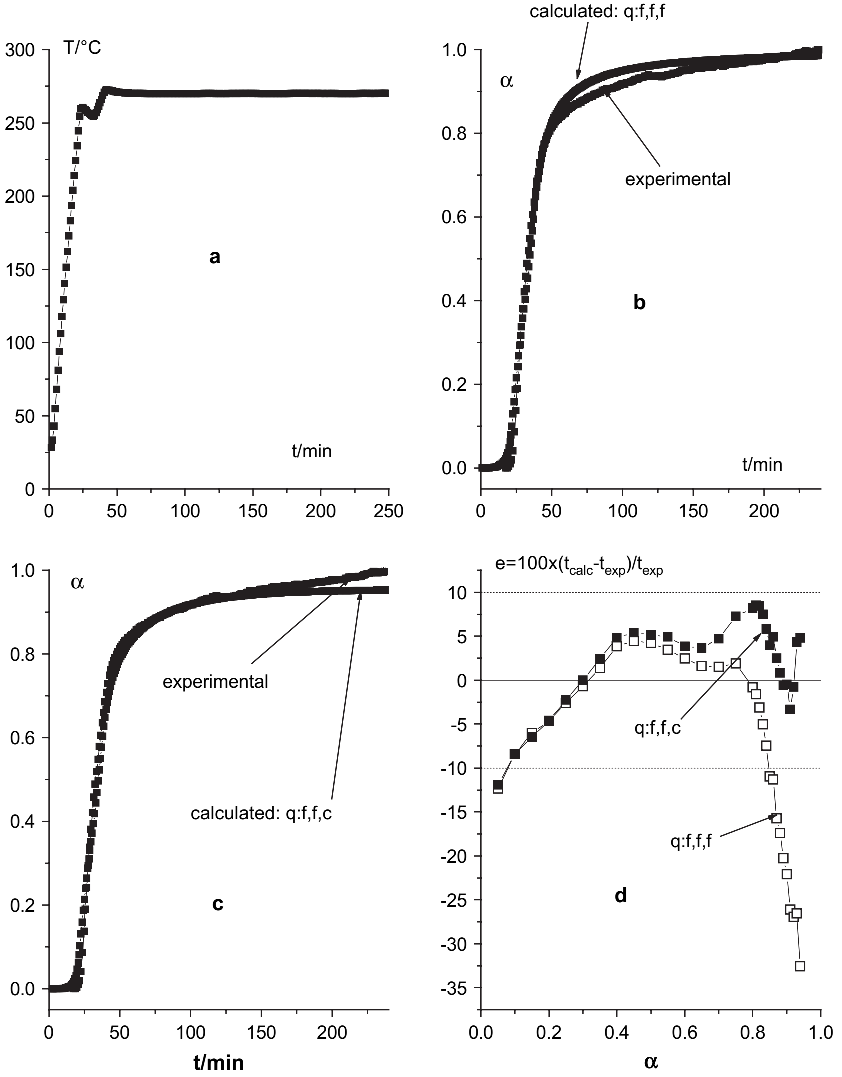

Fig. 9. (a) Temperature program in quasi-isothermal experiment. (b) Calculated (q:f,f,f scheme) and experimental TG curves for quasi-isothermal data. (c) Calculated (q:f,f,c scheme) and experimental TG curves for quasi-isothermal data. (d) The relative errors (e) in the time (t) evaluated for the two reaction schemes.

According to the results listed in Table 1, the best fit quality was obtained for the following schemes: q:f,f,c with the conversion functions An–An–An–Fn, and q:f,f,f with the conversion functions An–Fn–An–Fn. The corresponding kinetic parameters are listed in Table 2.

For these mechanisms, the experimental TG points lie practically on the regenerated curves (Figs. 5 and 6). However, for each DTG curve there is a good agreement among the experimental and simulated results only for the increasing portion and the first part of decreasing portion of this curve. This could be explained by the overlapping of process I with the following process of thermo-oxidation that occurs at relatively high temperatures.

In a previous paper [45] we suggest, as a necessary criterion for validity of the determined mechanism and the corresponding kinetic parameters, the good agreement between $E_{FR} = E_{FR}(\alpha)$ obtained from non-isothermal experimental data and $E_{iso} = E_{iso}(\alpha)$ obtained by applying the differential method to isothermal data simulated using non-isothermal kinetic parameters. In order to check this criterion, the isothermal data were calculated using data listed in Table 2, for nine temperatures in the range 170–250 °C with a step of 10 °C, and the dependence E_{iso} vs. α was determined. As one can see in Figs. 7 and 8, the curves E_{iso} vs. α are inside the range delimited by the standard deviations of E_{FR} for both the best mechanisms. Consequently, the above mentioned criterion is respected by the both best mechanisms.

The kinetic data listed in Table 2 were also used for calculation of the TG curve corresponding to the temperature program in which the quasi-isothermal experiment was performed (Fig. 9). It appears that the absolute value of the relative error in time (t) evaluation ($e = 100 \times ((t_{calc} - t_{exp})/t_{exp})$) is lower than 10% for q:f,f,c scheme in the range $0.10 \leq \alpha \leq 0.94$, and q:f,f,f scheme in the range $0.10 \leq \alpha \leq 0.84$. This result and F-test on fit-quality (Table 1) show that the best kinetic description of both non-isothermal and quasi-isothermal data is made by q:f,f,c scheme with the parameters given in Table 2. One notes that the best fitting of the non-isothermal experimental data, which are affected by inherent experimental errors, do not lead always to the real kinetic scheme and corresponding kinetic parameters that could be used for predictions. In a previous work [45], in which the results of the kinetic analysis of the complex thermo-oxidation degradation of poly(vinyl alcohol) were reported, it was obtained that not the kinetic scheme with the best F-test quality leads to a good agreement between an experimental and calculated TG curve. Therefore, in the application of “multivariate non-linear regression” program the obtained results must be checked by comparing an experimental and calculated TG curves corresponding to other temperature program

Table 3
The lifetime values of the investigated resin at different temperatures

$T/^\circ C$	Lifetime for 5% mass loss/h	Lifetime for 10% mass loss/h
130	1180	3030
135	735	1870
140	460	1175
145	295	740
150	190	475

than those used for the evaluation of the mechanism and kinetic parameters.

3.3. Lifetime prediction

The results of the kinetic analysis of the first process of thermo-oxidation of the investigated material can be used for thermal lifetime prediction at temperature higher than glass transition temperature and for mass loss as degradation criterion. As is recommended in IEC-216 Standard, 5% and 10% mass losses are the end-point criteria important for practical use of an epoxy resin used as electrical insulating material. The lifetime values for the investigated material, predicted using q:f,f,c scheme with corresponding kinetic parameters, are listed in Table 3. It is observed that at the considered temperatures, the lifetime is very sensitive to minor changes of temperature.

4. Conclusions

1. The processes which occur in the progressive heating in air of an epoxy resin obtained by curing of an industrially produced mixture of DGEBA with 4,4′-methylene-dianiline (MDA) were shown by thermal analysis (TG, DTG and DSC).
2. Kinetic analysis of the first process of thermo-oxidation was performed by isoconversional and “multivariate non-linear regression” program applied to the non-isothermal data recorded at five heating rates.
3. It was shown that the TG and DTG experimental points lie practically on the regenerated curves obtained using the kinetic parameters corresponding to the reactions schemes q:f,f,c and q:f,f,f.
4. The comparison of the experimental TG curve obtained in quasi-isothermal conditions ($T = 270\,^\circ C$) with the calculated TG curves for the above mentioned reaction schemes shows that q:f,f,c mechanism with corresponding calculated parameters is suitable for predictions.
5. The thermal lifetime values of the investigated epoxy resin at different temperatures and the end-point criteria 5% and 10% mass loss were evaluated.

Acknowledgements

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