# THERMOKINETIC STUDY OF THE THERMO-OXIDATIVE DEGRADATION OF A COMPOSITE EPOXY RESIN MATERIAL

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The thermo-oxidative degradation of a composite epoxy resin material used as electric insulator, obtained by mixing with quarz of a resin prepared by curing of an industrially produced RESIN 110S (a mixture of DGEBA with n=1 and DGEBA with n=2) with phtalic anhidride has been investigated by TG/DTG+DSC simultaneous analyses performed in static air atmosphere, at four heating rates. TG/DTG+DSC curves showed that, in the temperature range $25–750^0C$, the following processes succesively occur: an initial loss of some low molecular compounds resulted during material preparation (process I), a glass transition and two exothermic processes (II and III). The processing of the non-isothermal data corresponding to processes I and II was performed by using Netzsch Thermokinetic – A Software Module for Kinetic Analysis. The mechanisms and the corresponding kinetic parameters were determined by isoconversional and multivariate non-linear regression methods and checked for quasi-isotherma data ($T = 270^0C$).
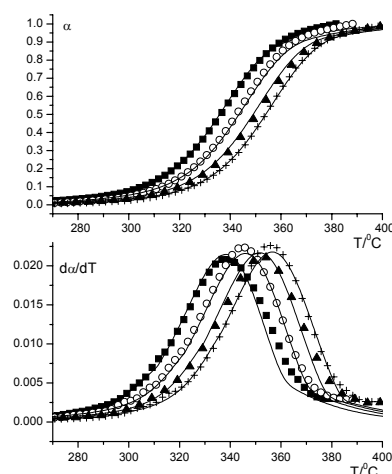
INTRODUCTION

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 determination of the degradation mechanisms and corresponding kinetic parameters. In many cases, the degradation of a polymeric material consists in their decomposition and/or thermo-oxidation with release of gaseous compounds, which can be investigated by the thermal analysis methods (TG/DTG, DTA, DSC, etc).

Experimental data for kinetic analysis of heterogeneous solid-gas reactions are often obtained in non-isothermal conditions, with a linear regime of temperature increase in time ($\beta = dT/dt$ = const., where β is the heating rate, T is the temperature and t is the time). Under such conditions, the methods for evaluation of kinetic parameters for a single step reaction are based on the rate equation:[1]

$$\beta\frac{d\alpha}{dT} = Af(\alpha)\exp\left(-\frac{E}{RT}\right) \qquad (1)$$

or its integral form:

$$g(\alpha) \equiv \int_0^\alpha \frac{d\alpha}{f(\alpha)} = \frac{A}{\beta}\int_0^T \left[\exp\left(-\frac{E}{RT}\right)\right]dT \qquad (2)$$

where: α is the conversion degree, A – the pre-exponential factor, E – the activation energy, $f(\alpha)$ – the differential conversion function, $g(\alpha)$ – the integral conversion function, and R - the gas constant.

According to these equations, a kinetic triplet (E, A, $f(\alpha)$ or $g(\alpha)$) describes the time evolution of a physical or chemical change. Obviously, a complex process is correctly described by a set of kinetic triplets.

Some relative critical analyses of the methods of evaluation of kinetic parameters from non-isothermal data[2-22] impose the conclusion that a correct determination of non-isothermal kinetic parameters involves the use of experimental data recorded at several heating rates. These data allow applying the model-free methods for evaluation of the dependence of the activation energy on the conversion degree, which can be correlated with the mechanism of the investigated process. The most used model-free methods are those suggested by Friedman[23] (FR method) and Ozawa, Flynn and Wall[24, 25] (OFW method). There are the following two cases: (1) E is independent on α; (2) E values change with α. In the first case, the investigated process is simple and is described from the kinetic point of view by a unique kinetic triplet. In the second case (E values change with α), the investigated process is complex (successive, parallel, reversible reactions), and, consequently, it is described by a set of kinetic triplets.

For a complete kinetic description of the investigated process, the all members of a kinetic triplet for a single step process or triplets for a multi-steps process should be determined. The following software packages only available for commercial use were drawn up particularly for kinetic analysis of non-isothermal and isothermal data: TA-KIN for Windows v. 1.6 (Anderson et al.);[26] NETZSCH Thermokinetics software (Opfermann);[27] KINETICS for Windows 95/98/NT

(Burnham and Braun);[28] ATKS for Windows 95-98 (Roduit).[29] The final test of every kinetic analysis should be to use the determined parameters to construct calculated curves for comparison with the experimental results over a wide and representative range.[15] On this last necessary condition there are based some procedures for kinetic parameters evaluation from non-isothermal data, like the above mentioned software packages[26-29] and DTG fitting method.[30, 31]

The above mentioned procedures for kinetic analysis of non-isothermal data were previously used for investigation of some polymers which are the main components of some electric insulators (PVC[32], epoxy resin[33], HDPE[18]). The aim of this work has been the use of these procedures for kinetic analysis of non-isothermal data obtained by simultaneous TG/DTG+DSC analysis of a composite epoxy resin material used as electric insulator.

EXPERIMENTAL

Materials

The used row materials were: Resin 110S (a mixture of DGEBA with n=1 and DGEBA with n=2) produced by Policolor-Bucharest-Romania; phthalic anhydride (purity 99.5%) produced by VEGA-Ploiesti-Romania, and quartz sand powder type 1(minimum 97.5% SiO_2; granulation in the range 0.1 – 0.4 mm) produced by Silirom-SA-Orsova-Romania). A mixture of resin 110 S and phthalic anhydride in the ratio 92.5:7.5 was heated at 90^0C up to an homogeneous mass was obtained. Then the quartz sand powder was added in the ratio 1:1, and the obtained mixture was heated at 120^0C for 24 h. The obtained material exhibits a high electric rigidity (12 kV.mm^{-1}) and therefore is used as electric insulator.

Thermal analysis

The heating curves (TG, DTG and DSC) of the investigated material were simultaneously recorded with STA 490 C apparatus produced by Netzsch-Germany, in static air atmosphere, in the temperature range 25^0C…750^0C, at the following heating rates: 5.02; 7.56; 10.10 and 12.98 K.min^{-1}, and using Pt-Rh crucible. The sample mass was in the range 16.0 – 16.6 mg.

In order to check the mechanism and corresponding kinetic parameters, the thermal analysis of the material was also performed in static air atmosphere and the following temperature program (quasi-isothermal program for $T = 270^0$C):

$$23.6^0C \xrightarrow{10.88K/min} 259.6^0C \xrightarrow{1.50K/min} 261.3^0C \xrightarrow{-0.78K/min} 254.6^0C \xrightarrow{2.18K/min} 272^0C \rightarrow$$

$$\xrightarrow{0.62K/min} 272.8^0C \xrightarrow{-0.21K/min} 270^0C \xrightarrow{284.7min} 270^0C$$

Processing of the experimental data

"Netzsch Thermokinetics – A Software Module for the Kinetic Analysis of Thermal Measurements" was used for processing the non-isothermal data and the comparison of the calculated and experimental curve corresponding to quasi-isothermal experiment. This program allows evaluating the dependence of E on α by means of FR and OFW model-free methods, and the determination of the complex mechanism of the investigated process and the corresponding kinetic parameters. Recently[18, 32-47] this program was used for kinetic analysis of some non-isothermal data.

RESULTS AND DISCUSSION

Fig. 1 shows the simultaneous obtained TG, DTG and DSC curves for the investigated material, recorded at 12.98 K.min^{-1}; similar curves were obtained for all heating rates.

According to these TG, DTG and DSC curves, the following processes occur at the progressive heating of the composite material: a glass transition characterized by $T_g = 114^0$C, and three global processes with formation of volatile compounds, namely the endothermic process denoted by I consisting in the loss of some low molecular compounds resulted during material preparation, and two exothermic processes denoted by II and III. The mass of the white residue evaluated from TG curves is practically equal with the mass of added quartz sand (49.05±0.26 %). For the heating rates 5.02; 7.56; 10.10 and 12.98 K.min^{-1}, the mass losses were: in process I: 2.88%; 2.61%; 2.62%; 2.71%; in process II: 26.51%; 26.87%; 27.24%; 27.12%; in process III: 21.53%; 21.66%; 20.72%; 21.29%. The good agreement among the mass losses observed at different heating rates shows that the investigated material is homogeneous.
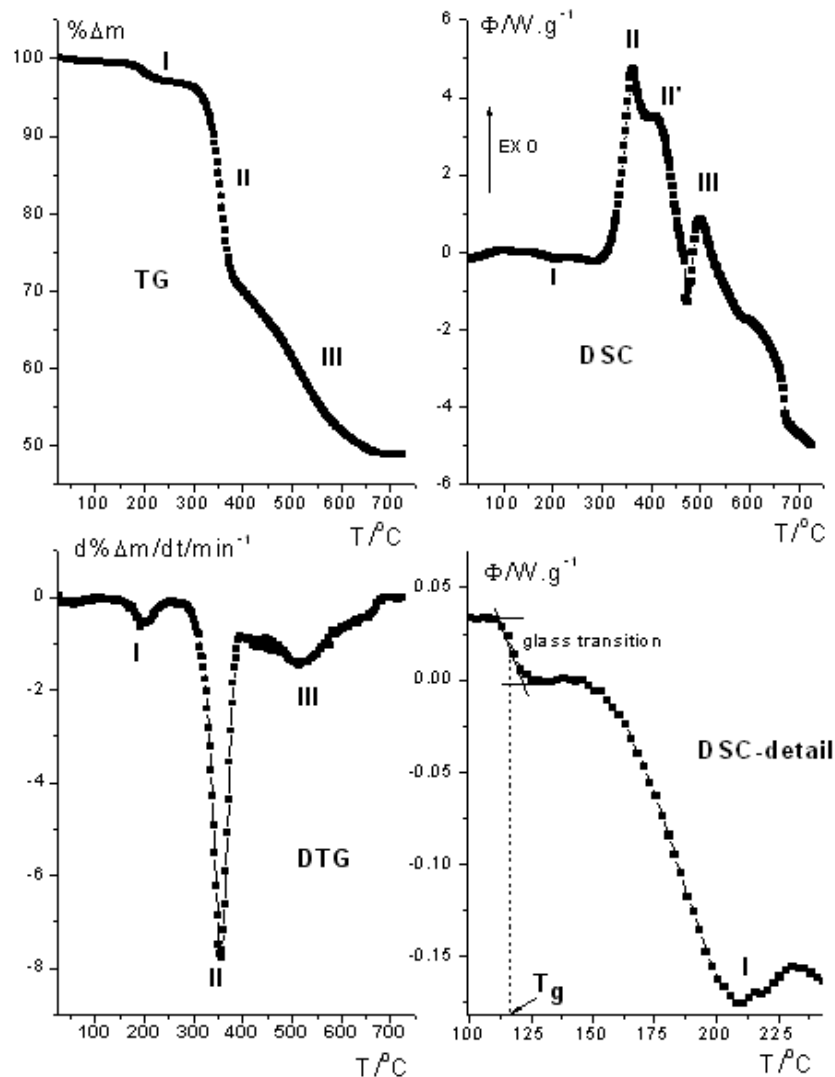

Fig. 1 – TG, DTG and DSC curves for the composite epoxy resin material heated in static air atmosphere, at the heating rate of 12.98 K. min^{-1}.
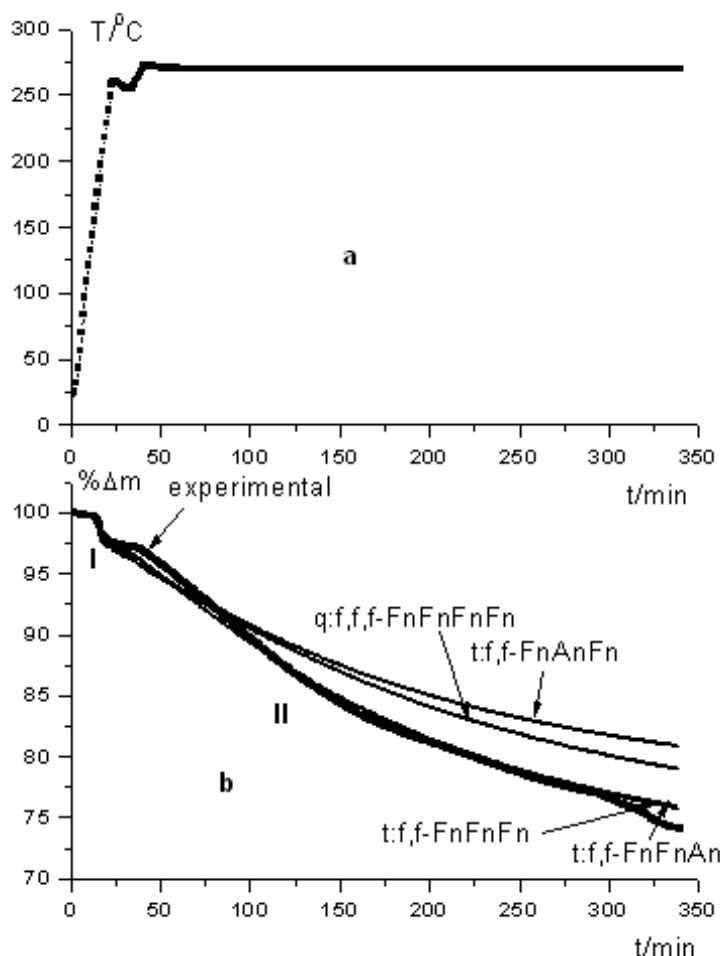
Fig. 2 – Quasi-isothermal experiment: (a) temperature program; (b) TG curves: thick line – experimental data;
thin lines correspond to simulated TG curves for the most probable four mechanisms of the process II.

The results obtained in quasi-isothermal experiment ($T = 270{}^0C$) are shown in Fig. 2. The analysis of the data obtained in both non-isothermal and quasi-isothermal conditions has revealed the following: (i) the mass loss in quasi-isothermal conditions corresponds to the process denoted by I and II in Fig. 1; (ii) in quasi-isothermal conditions, the duration of process I is substantially lower than that of process II; (iii) in both experimental conditions, the processes I and II are well separated.

The kinetic analysis was performed for processes I and II, characterized by above mentioned mass losses.

Model-free estimation of the activation energy

The analysis of the results obtained by application of FR and OFW methods (Fig. 3) has revealed the following: (i) for both processes, E_{FR} and E_{OFW} change with the conversion degree; (ii)

for process II and $\alpha > 0.32$, both E_{FR} and E_{OFW} exhibit values of the relative standard deviation higher than 10%; (iii) for each process, there are differences between E_{FR} and E_{OFW} values, which are explained[48] by the relations that ground the model-free methods.

In the following, we will refer to results obtained by FR method that, unlike OFW method, uses the point values of overall process rate, and therefore these do not depend on the system history in the range $0 - \alpha$.

Application of multivariate non-linear regression program

The above remarks concerning the results obtained by model-free methods show that both processes I and II are complex. In order to find the mechanisms of these processes and the corresponding kinetic triplets, we used multivariate non-linear regression program included by

"Netzsch Thermokinetics" software. This program is based on multiple heating rates, and makes the assumption that the kinetic parameters are identical for measurements at all heating rates. The procedure was performed to obtain the formal kinetic model to be used in predictions. This aim corresponds to the "technical aspect" of non-linear regression analysis, according to which the kinetic analysis is examined as a tool for data reduction.[27] The non-isothermal data recorded at the above mentioned four heating rates were brought together during analysis and the relevant differential equations of the reaction rates were solved numerically, and the kinetic parameters were optimized iteratively.

The calculations were performed in the range of the $0.05 \leq \alpha \leq 0.90$ conversion degree and considering the following conversion functions:

- reaction order model, Fn: $f(\alpha) = (1-\alpha)^n$ (n is the reation order);
- n^{th} order reaction with autocatalysis, Cn: $f(\alpha) = (1-\alpha)^n (1+K_{cat}\alpha)$;
- Avrami-Erofeev model, An: $f(\alpha) = n(1-\alpha)\left[-\ln(1-\alpha)\right]^{(1-1/n)}$ (n is a constant parameter).

Some reaction schemes given in the "Netzsch Thermokinetics" program and consisting in consecutive, parallel and/or reversible reactions were taken into account. The values of E vs. α obtained by FR isoconversional method were used as starting parameters for non-linear regression model-fitting procedure.

The analysis of the non-isothermal data corresponding to process I shows that this is satisfactory described by the scheme p:f,f,f,f with the kinetic models Fn-An-Fn-An-Fn: $A-1 \rightarrow B-2 \rightarrow C-3 \rightarrow D-4 \rightarrow E-5 \rightarrow F$ (the codifications are those used in "Netzsch Thermokinetics" program; A, B, C, D, E and F are solid compounds; 1; 2; 3; 4 and 5 denote the mechanism steps). The corresponding kinetic parameters are listed in Table 1. As will be shown below, this mechanism gives also a good kinetic description of the quasi-isothermal experimental data. As was above mentioned, both the total mass loss in process I as well as the duration of this process is substantially lower than those corresponding to process II. Therefore, in the following we will focus to the kinetic analysis of process II.
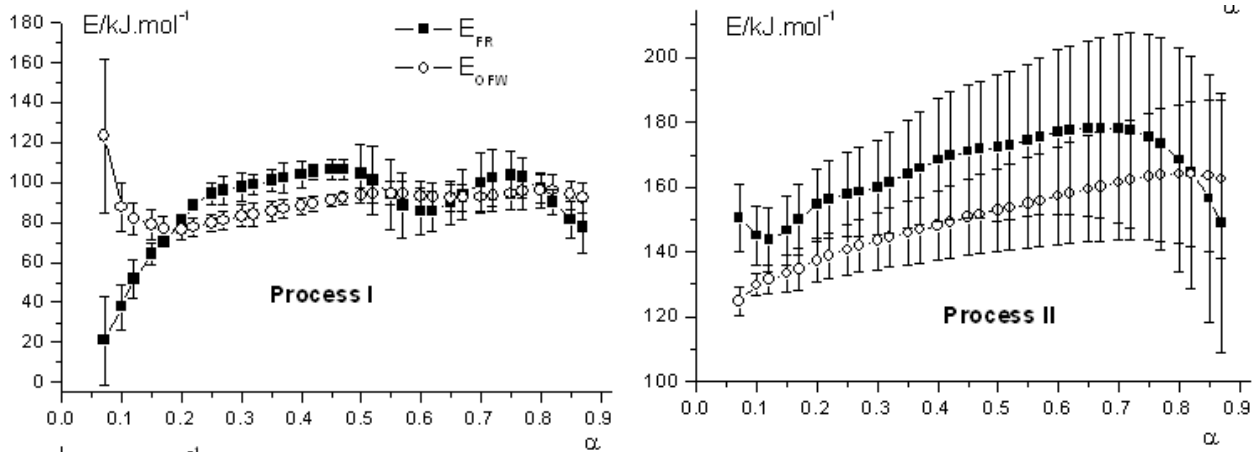

Fig. 3 – Dependencies of the activation energy evaluated by model-free methods on the conversion degree.

Table 1

Non-isothermal kinetic and statistic parameters after non-linear regression through
the most probable mechanisms of the process I

p:f,f,f,f with the kinetic models Fn-An-Fn-An-Fn		Statistic parameters	
Parameter	Value	Parameter	Value
$\log A_1/s^{-1}$	6.425	Correlation coefficient	0.99901
$E_1/kJ.mol^{-1}$	74.1	Durbin-Watson factor	2.161
n_1	0.368	t-critical (0.95; 83)	1.980
$\log A_2/s^{-1}$	14.950		
$E_2/kJ.mol^{-1}$	101.3		
n_2	4.000		

Table 1 (continued)

$\log A_3/s^{-1}$	8.404
$E_3/kJ.mol^{-1}$	94.1
n_3	1.566
$\log A_4/s^{-1}$	11.017
$E_4/kJ.mol^{-1}$	94.3
n_4	4.000
$\log A_5/s^{-1}$	10.858
$E_5/kJ.mol^{-1}$	77.1
n_5	1.311
FollReact 1[a]	0.102
FollReact 2[b]	0.237
FollReact 3[c]	0.030
FollReact 4[d]	0.300

[a,b,c,d] Share of reaction step i (i=1; 2; 3; 4) in the total process; The share of step 5 (E→F) is given by $1 - \sum (foll\,React)$

For finding the mechanism of process II, we compared the F-test on fit-quality values and the "mean absolute relative difference" between the calculated and experimental values (*ARD*), given for a quantity *q* by the relation:

$$ARD = \frac{100}{N} \sum_N \left| \frac{q_{exp} - q_{calc}}{q_{calc}} \right| \qquad (3)$$

where *N* is the number of considered values of *q*.

The results obtained for the four most probable mechanisms according to F-test on fit-quality and *ARD* for α and (dα/d*T*) values are shown in Table 2. The corresponding kinetic parameters are listed in Table 3. In the limits of inherent experimental errors, for all of these mechanisms, close values of *ARD* for α and (dα/d*T*) were obtained, and experimental TG and DTG points lie practically on the regenerated curves (this is illustrated in Fig. 4 for the mechanism t:f,f ($A - 1 \to B - 2 \to C$) with kinetic models Fn-An-Fn; similar results were obtained for all four considered mechanisms).

Table 2

F-test on fit quality and *ARD* values for some quantities

F-test on fit quality									*ARD* for		
Nr.	Code	Fexp	Fcrit (0.95)	f-act	Type-1	Type-2	Type-3	Type-4	α* %	dα/dT* %	t_{q-i}** %
0	t:f,f	1.00	1.41	94	Fn	An	Fn		3.09	4.03	24.4
1	q:f,f,f	1.02	1.41	94	Fn	Fn	Fn	Fn	2.81	3.61	11.3
2	t:f,f	1.31	1.41	93	Fn	Fn	An		3.89	4.58	4.1
3	t:f,f	1.56	1.41	94	Fn	Fn	Fn		3.64	5.55	4.4

* *ARD* was evaluated for 0.05<α<0.87; ** t_{q-i} = time in quasi-isothermal experiment

Table 3

Non-isothermal kinetic and statistic parameters after non-linear regression through the most four probable mechanisms of the first thermo-oxidation process II of the investigated material

t:f,f with the kinetic models Fn-An-Fn		q:f,f,f with the kinetic models Fn-Fn-Fn-Fn		t:f,f with the kinetic models Fn-Fn-An		t:f,f with the kinetic models Fn-Fn-Fn	
Parameter	Value	Parameter	Value	Parameter	Value	Parameter	Value
$\log A_1/s^{-1}$	6.752	$\log A_1/s^{-1}$	8.435	$\log A_1/s^{-1}$	7.418	$\log A_1/s^{-1}$	8.389
$E_1/kJ.mol^{-1}$	100.0	$E_1/kJ.mol^{-1}$	118.0	$E_1/kJ.mol^{-1}$	100.0	$E_1/kJ.mol^{-1}$	118.0
n_1	0.493	n_1	0.847	n_1	0.934	n_1	0.920
$\log A_2/s^{-1}$	10.937	$\log A_2/s^{-1}$	11.337	$\log A_2/s^{-1}$	10.865	$\log A_2/s^{-1}$	10.871
$E_2/kJ.mol^{-1}$	155.0	$E_2/kJ.mol^{-1}$	155.0	$E_2/kJ.mol^{-1}$	155.0	$E_2/kJ.mol^{-1}$	155.0
n_2	1.363	n_2	0.936	n_2	1.110	n_2	1.017
$\log A_3/s^{-1}$	8.054	$\log A_3/s^{-1}$	12.694	$\log A_3/s^{-1}$	8.474	$\log A_3/s^{-1}$	8.188
$E_3/kJ.mol^{-1}$	120.0	$E_3/kJ.mol^{-1}$	175.0	$E_3/kJ.mol^{-1}$	120.0	$E_3/kJ.mol^{-1}$	110.0
n_3	0.565	n_3	1.453	n_3	1.970	n_3	2.000
FollReact 1	0.069	$\log A_4/s^{-1}$	8.893	FollReact 1	0.079	FollReact 1	0.048

Table 4 (continued)

FollReact 2	0.900	E_4/kJ.mol^{-1} n_4 FollReact 1 FollReact 2 FollReact 3	110.0 2.000 0.052 0.244 0.622	FollReact 2	0.683	FollReact 2	0.800
Statistic parameters			Statistic parameters			Statistic parameters			Statistic parameters		
r	D-W	t-cr (0.95; 87)	r	D-W	t-cr (0.95; 91)	r	D-W	t-cr (0.95; 86)	r	D-W	t-cr (0.95; 88)
0.99912	4.296	1.979	0.99908	5.634	1.977	0.99870	5.916	1.979	0.99841	5.332	1.978

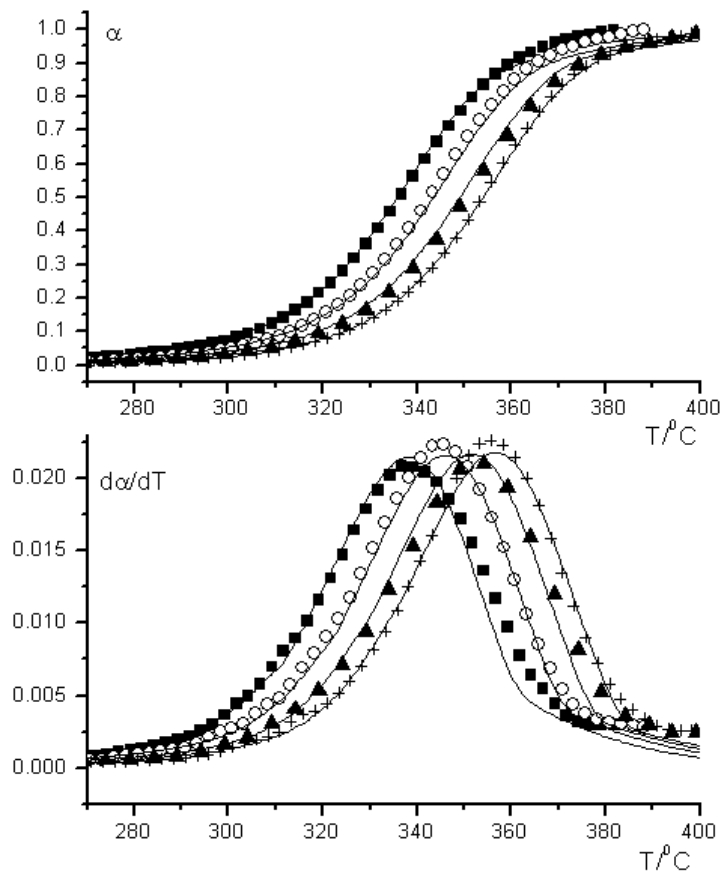r = correlation coefficient; D-W = Durbin-Watson factor; t-cr = t-critical

Fig. 4 – Fit of the measurements through three step mechanism t:f,f with the conversion functions Fn-An-Fn.
Experimental: ■ 5.02 K.min^{-1}; o 7.56 K.min^{-1}; ▲ 10.10 K.min^{-1}; + 12.98 K.min^{-1}. Calculated: continous line.

The kinetic data listed in Tables 1 and 3 were also used for calculation of TG curve corresponding to the temperature program in which the quasi-isothermal experiment was performed (Fig. 2). An unexpected result was obtained, namely the experimental TG points corresponding to quasi-isothermal experiment lie on the regenerated TG curves only for the two mechanisms that exhibit the third and fourth positions in the order of decreasing of F-test on fit-quality. Consequently, for these two mechanisms, *ARD* values for t_{q-I} (time in quasi-isothermal experiment) are substantially lower than those for

mechanisms with a better F-test on fit-quality (see Table 2). These results show that the application of above mentioned statistical criteria for processing of non-isothermal data recorded at several heating rates does not lead always to the true mechanism of a complex process and corresponding true kinetic parameters, which can be used for predictions. A similar result was reported in a previous recent papers[18, 38], according to which the best F-test on fit quality does not lead to the true kinetic scheme of poly(vinyl alcohol) (PVA)[38] and UHDPE[18] degradations.

The results presented in these paper confirms the algorithm of kinetic analysis of heterogeneous processes previously suggested,[18] according to which the following successive steps must be performed for the correct determination of mechanism and the corresponding kinetic parameters:

(1) application of a model-free method for evaluation of E vs. α;

(2) use of liniar and nonlinear regression programs that are associated with some statistical criteria for evaluation of the most probable mechanisms and corresponding kinetic triplets;

(3) checking the agreement between experimental and calculated α vs. t curves recorded in some temperature programs other than those used in assessing the kinetic parameters.

CONCLUSIONS

By thermal analysis (TG, DTG and DSC) performed at four heating rates, there were put in evidence the processes that occur at the progressive heating in air of a composite epoxy resin material used as electric insulator, obtained by mixing with quarz of a resin prepared by curing of an industrially produced RESIN 110S (a mixture of DGEBA with n=1 and DGEBA with n=2) with phtalic anhydride.

The kinetic analysis of the first two degradation processes was performed by isoconversional and "Multivariate non-linear regression" program applied to the non-isothermal data recorded at four heating rates.

It was pointed out that the first degradation process exhibits p:f,f,f,f reactions scheme with the kinetic models Fn-An-Fn-An-Fn.

For the second degradation process, the TG and DTG experimental points lie practically on the regenerated curves obtained using the kinetic parameters corresponding to the following reactions schemes: t:f,f with the kinetic models and order of decreasing of F-test on fit-quality Fn-An-Fn, q:f,f,f with the kinetic models Fn-Fn-Fn-Fn, t:f,f with the kinetic models Fn-Fn-An and t:f,f with the kinetic models Fn-Fn-Fn.

The comparison of the experimental TG curve obtained in quasi-isothermal conditions (T=270^{0}C) with the calculated TG curves for the above mentioned reaction schemes shows that only t:f,f with the kinetic models Fn-Fn-An and t:f,f with the kinetic models Fn-Fn-Fn.reaction schemes with corresponding calculated parameters are suitable for predictions.

The obtained results confirm the necessity of checking the agreement between experimental and calculated α vs. t curves recorded in some temperature programs other than those used in assessing the kinetic parameters for correct determination of the mechanism and the corresponding kinetic parameters of a complex process from non-isothermal data.

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