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KINETICS OF NON-ISOTHERMAL DECOMPOSITION OF THREE IRGANOX-TYPE ANTIOXIDANTS

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In the present work a comparative kinetic study was performed on the thermal behavior of three antioxidants of IRGANOX-type (L101, L109 and L115) in dynamic air atmosphere under non-isothermal conditions.

The TG-DTG data were obtained at heating rates of 5, 7, 10 and 15 K min^{-1}. The kinetic parameters were obtained by processing these data with strategies corresponding to Flynn–Wall–Ozava (FWO), Friedman (FR), Budrugeac–Segal (BS) and non-parametric kinetic (NPK) methods.

The thermal degradation by all the three compounds take place in melted state, so that any kinetic models regarding the decomposition of solids are inapplicable. Only with the NPK method it was possible a separation between the two functions of the reaction rate.

For the temperature dependence, *f*(*T*), an Arrhenius-type model was searched; for the conversion dependence, the Šestak–Berggren equation was suggested in order to discriminate between physical (m) and chemical (n or p) steps of a complex thermodegradation process.

Keywords: *antioxidants, non-isothermal kinetics, NPK method*

Introduction

The antioxidants are compulsory additives in each polyurethane composition. These are of two types: reactive antioxidants, which are inserted in the polymeric chain during the synthesis, and mixture antioxidants, incorporated in the bulk polymer. The last one has the advantage of no influence on the designed properties of the polyurethane.

In a recent paper [1], the effect of antioxidants and stabilizators on different polyurethanes was evaluated by kinetic analysis of DSC data.

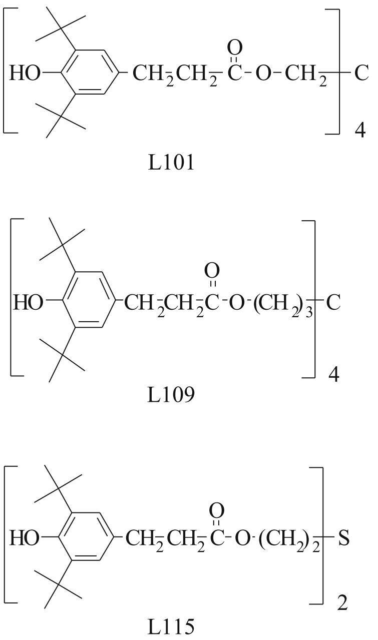
Following the topic of our previous work [2], the aim of this paper is to present a kinetic study on the decomposition of IRGANOX-type antioxidants, in order to estimate the antioxidant properties of these compounds before using into a polyurethanes recipe.

IRGANOX is a 'Ciba' trade mark for a series of phenolic antioxidants initially developed as additives for lubricants.

Experimental

The studied compounds were IRGANOX L101, L109 and L115 (Fig. 1).

By this compounds, the phenol group is steric hindranced by two *t*-butyl groups in the neighboring positions.



L101

L109

L115

Fig. 1 Chemical structure of the studied IRGANOX-type compounds

The thermal analysis was carried out on a Perkin Elmer DIAMOND devices, in dynamic air atmosphere (100 mL min^{-1}) and heating rates of 5, 7, 10 and 15 K min^{-1}.

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Table 1 The thermooxidative characteristics of the IRGANOX samples

IRGANOX-type	Mass loss/%	Initial temp./°C	Final temp./°C	Max. of DTG/°C	Max. of DTA/°C	Melting point/°C
L101	68.1	335	380	365	Exo 375	115
L109	90.8	312	360	340	Exo 360	105
L115	95.0	320	365	355	Exo 365	70

Results and discussions

Thermoanalytical data

Examples of the three thermoanalytical curves, i.e. TG, DTG and DTA are depicted in Fig. 2. The main data are presented in Table 1.

Some comments are necessary:

- the first observed thermal phenomenon is the melting; the maximum of the corresponding endothermic DTA peak is in concordance with the value indicated by the producer (CIBA);
- the degradation is due to a thermooxidative process (exothermic effect) and takes place at temperatures significant higher than the melting point;
- the values of the relative mass loss by L109 and L115 are rather the same and very different from the value for L101.

Kinetic analysis

1. The Flynn–Wall–Ozawa (FWO) [3, 4] isoconversional method, is a model-free method based on the rate equation in non-isothermal conditions, written like

$$\ln\beta = \ln A\left[\frac{f(\alpha)}{\mathrm{d}\alpha/\mathrm{d}T}\right]_{\alpha} - \frac{E}{RT} \qquad (1)$$

where α – degree of conversion, β – heating rate, A – pre-exponential factor in the Arrhenius equation, E – activation energy, R – gas constant, T – temperature and $f(\alpha)$ – non-defined differential conversion function.

By plotting $\ln\beta$ *vs.* $1/T$ at α=const., a family of straight lines with the slope $-E/R$ will be obtained.

The results i.e. E *vs.* α diagrams are depicted in Fig. 3. Despite of a too large variation of E *vs.* α, two observations are noticeable: i) According to Vyazovkin and Lesnikovich [5], the peculiar shape of E *vs.* α variation is associated with a complex reaction process (by L115 especially). ii) By L101 and L109 it is a range, between α=0.1 and 0.7 with a relative constant value of E.

Anyhow, the kinetic study should be continuing with another data processing methods.

2. The differential-isoconversional method by Friedman [6] is based on the equation:

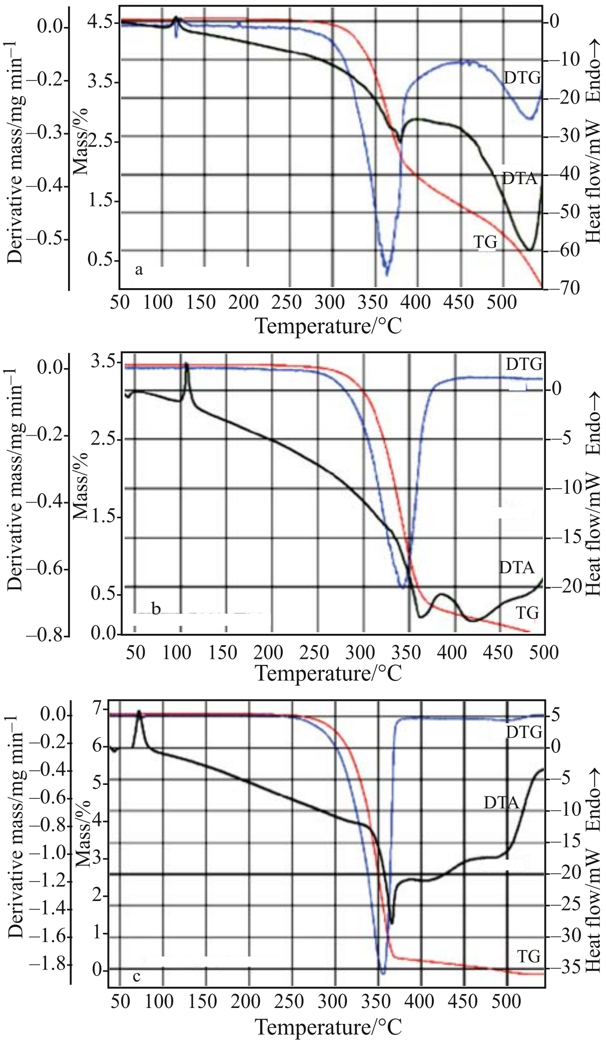

Fig. 2 Thermoanalytical curves at heating rate of 10 K min^{-1} for a – L101; b –109; c – L115

$$\left(\beta\frac{\mathrm{d}\alpha}{\mathrm{d}T}\right)_{\alpha} = Af(\alpha)\exp\left(-\frac{E}{RT}\right) \qquad (2)$$

At a certain conversion, the slope and the intercept of the straight line of $\ln(\beta\mathrm{d}\alpha/\mathrm{d}T)$ *vs.* $1/T$ give the activation energy and the product $Af(\alpha)$ respectively. By simple single-step processes, the obtained values of E are invariant in respect of α.

The data obtained are summarized in Table 2, and it is obvious that the value of the standard

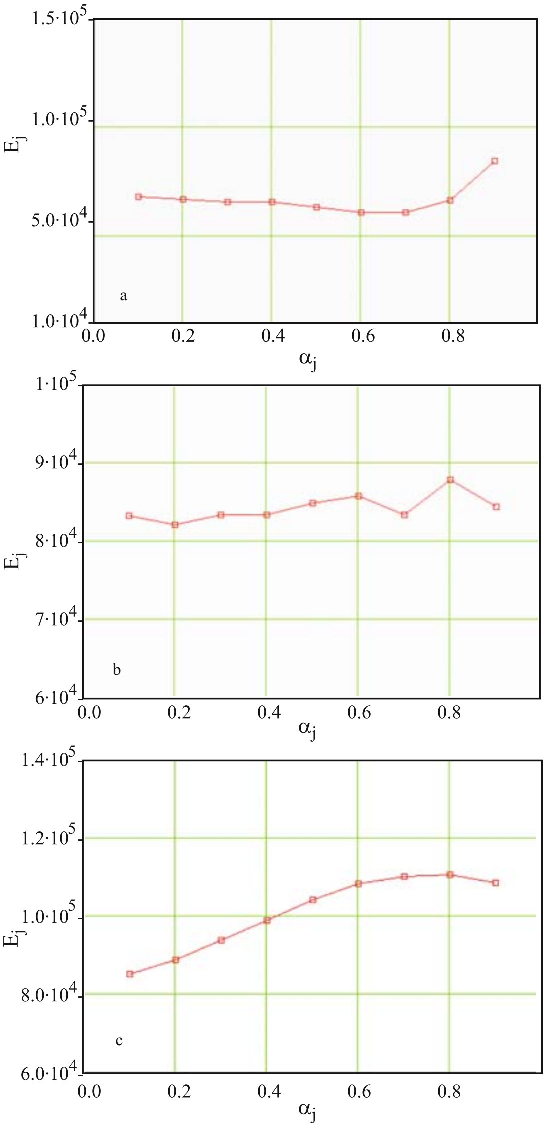

Fig. 3 Variation of activation energy *vs.* conversion, according to FWO method a – IRGANOX L101, b – IRGANOX L109, c – IRGANOX L115

deviation *s* is too high for considering *E* as invariant in respect of α. Therefore, more sophisticated methods for the data processing are necessary.

3. The Budrugeac–Segal [7–9] method is often useful for description and simulation of complex processes [2, 10–14].

This method is, logically, a continuation of Friedman's method, but in our case it is not applicable because one of the hypotheses related to this method is not fulfilled, namely a logarithmic dependence of *E* *vs*. α:

$$E=E_0+E_1\ln(1-\alpha) \quad (3)$$

4. Non-parametric kinetic (NPK) method [15–17] is a more sophisticated method based on the hypothesis that the reaction rate *r* can be expressed as a product of two independent functions, *f*(*T*) and *g*(α). So, the experimental points, obtained at different heating rates, are represented in a 3D coordinate system (*r*, *T*, α) and then interpolated as a continuous surface of the reaction rate. This surface is discretizated as a square matrix M which is decomposed, using the singular value decomposition algorithm [18], into

$$\mathrm{M}=\mathrm{U}(\mathrm{diagS})\mathrm{V}^{\mathrm{T}} \quad (4)$$

The first column of matrix U gives a vector u_1 that is analyzed *vs*. dependence on α; for this conversion function the Šeštak–Berggren (SB) equation [19] was suggested:

$$g(\alpha)=\alpha^{m}(1-\alpha)^{n}[-\ln(1-\alpha)]^{p} \quad (5)$$

A similar vector v_1, corresponding to matrix V is checked for an Arrhenius type temperature dependence.

By a simultaneous multistep process, the matrix M became a sum

$$\mathrm{M}=\sum_i \mathrm{M}_i \quad (6)$$

each matrix M_i generates a pair of descriptive vectors u_{1i} and v_{1i}. The contribution of each step *i* to the whole observed process is estimated by the explained variance λ_i, so that $\Sigma\lambda_i=1$.

The results of the NPK analysis are presented in Table 3.

By inspecting the data in Table 3 and taking into account the data processing strategy of the NPK method, the following observations are noticeable:

- The separation between the temperature, respective conversion dependence was achieved and the conversion function was established without any a priori hypothesis or approximations;
- A separation of the simultaneous steps of a complex process was possible. By L101 there are two such steps, a principal (λ=0.75) and a secondary (λ=0.25) respectively. By L109 and

Table 2 Activation energy, kJ mol^{-1}, *vs*. conversion, by Friedman's method

Sample	Conversion α										
	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	Main *E*	Standard dev. *s*/%
L101	84.9	82.0	82.8	79.1	76.3	80.0	88.9	112.8	133.6	91.1	62.9
L109	114.7	119.6	120.1	117.9	116.3	114.2	107.8	116.7	106.4	114.8	11.9
L115	119.3	120.6	134.8	143.3	150.0	157.9	154.3	157.3	136.4	141.5	27.3

Table 3 The kinetic parameters by NPK method

Sample	Explained variance, λ/%	Activation energy, E/kJ mol^{-1}	Pre-exponential factor, A/min^{-1}	Šesták–Berggren coefficient			$\bar{E}=\sum E_i\lambda_i$
				m	n	p	
L101	0.75	80.2	$8.84\cdot10^5$	0	2	1	99.8
	0.25	158.8	$2.84\cdot10^{12}$	0	2	2/3	
L109	0.91	88.8	$1.06\cdot10^7$	–	1/2	–	94.7
L109	0.90	116.9	$2.31\cdot10^9$	–	0.2	–	119.1

L115 the value of $\lambda\geq90\%$ is a consistent argument for considering a single-step process.

- The decomposition mechanism involve only chemical phenomena, i.e. transformations which implies the remainder reactant $(1-\alpha)$. Indeed, the SB coefficients are $m=0$, respectively n, $p\neq0$. This is in agreement with reaction kinetics in liquid/melted state [20].

Conclusions

- The kinetics of thermooxidative degradation under non-isothermal conditions of three IRGANOX-type antioxidants was studied;
- Four methods for the kinetic analysis of the thermoanalytical data were used;
- The NPK method offers two major advantages: a) the possibility of separation of two or more steps of a complex decomposition reaction; b) the possibility of discrimination between the conversion, respective the temperature dependence of the rate equation;
- The decomposition occurs in melted state and the kinetic model agrees with a homogeneous decomposition of a pure condensed phase;
- Within the values of the kinetic parameters, IRGANOX L109 seems to have the better antioxidant properties, due to low activation energy and appropriate conversion dependence.

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