

PROCESSING OF NON-ISOTHERMAL TG DATA Comparative kinetic analysis with NPK method

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Due to the criticism of the non-isothermal kinetic at a single heating rate, in the last period, data obtained at different heating rates are processed by means of elevated methods like Friedman's (FD) differential–isoconversional method or the one suggested by Budrugeac and Segal (BS).

The non-parametric kinetics (NPK) method, suggested by Serra, Nomen and Sempere offers two major advantages: the possibility of separation of two or more steps of a complex decomposition reaction; and the possibility of discrimination between the conversion, with regard to the temperature functions of a rate equation.

Comparative data of FD, BS and modified version of NPK method are presented for decomposition of three compounds used as polyisocyanate stabilizer.

Keywords: compensation effect, isoconversional methods, non-isothermal kinetics, non-parametric kinetics (NPK)

Introduction

In the last years, the kinetic data obtained under non-isothermal conditions at a single heating rate were critically evaluated [1]. The main objections were the variation of the activation energy (E) vs. both heating rate (β) and the degree of conversion (α).

Therefore, the recent ICTAC 2000 Project [2] suggests some methods for processing the thermogravimetric (TG) data obtained at different heating rates.

In this paper we attempt a comparative kinetic analysis of data obtained by using the Friedman's differential isoconversional method [3], the Budrugeac and Segal method [4–6] and a modified non-parametric kinetics (NPK) method (after Serra, Nomen and Sempere [7–9]). The TG studies were performed on a series of bis-urethanes as important stabilizers of polyurethane [10]. For the kinetic studies a well-characterized structure of a molecule with rather high molar mass and the thermal decomposition after melting and a single step TG curves is presented [10].

Experimental

Thermal analysis

TG and DTG curves were obtained using a Perkin-Elmer TGA7 Thermobalance, in dynamic nitrogen atmosphere (20 mL min^{-1}), at heating rates of 7, 10, 12 and 15 K min^{-1} .

Synthesis

The compounds were synthesized by an addition of a cyclic hydroxyl derivatives to toluylene-2,4-diisocyanate. The reaction takes place in hexane, under 4 h of refluxing, with tin-dibutyl-dilaurate as catalyst. After synthesis, the product was filtered and purified with recrystallization from dimethyl-formamide. The synthesis data are collected in Table 1.

Results and discussion

In Fig. 1 TG and DTG curves are presented. It is remarkable that all compounds exhibit one main decomposition step after melting. This means that by thermal decomposition in a fluid state no nucleation or diffusion-controlled processes should be occurred.

Processing of the TG data using the isoconversional method

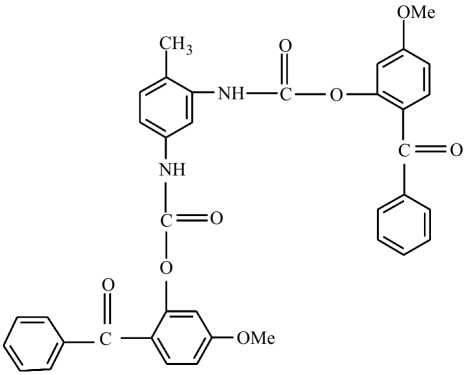
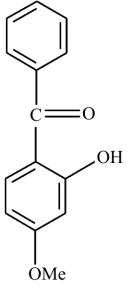
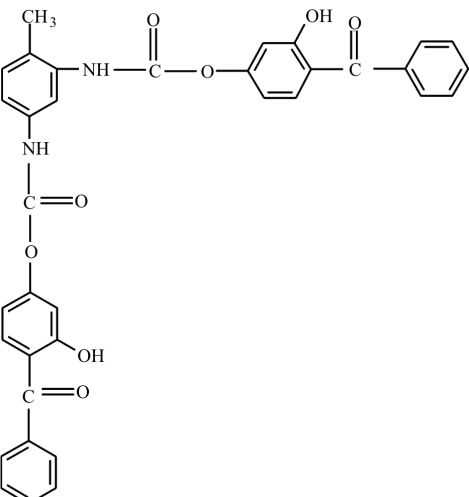
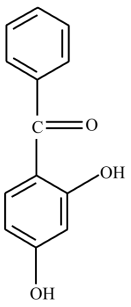
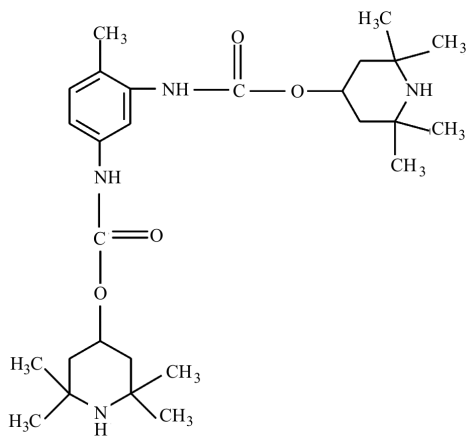
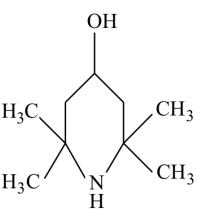
From the generally accepted equation of the non-isothermal kinetics

$$\beta \frac{d\alpha}{dT} = f(\alpha) A \exp\left(-\frac{E}{RT}\right) \quad (1)$$

where β is the heating rate and T is the temperature in K, the equation corresponding to the Friedman's differential isoconversional method [3], was obtained

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Table 1 Synthesis of the addition compounds

Sample	Addition reactant	Melting range/°C	Yield/%
 <p>Sample I $C_{37}H_{30}O_8N_2$</p>	 <p>UVASORB MET (Sigma)</p>	107–110	46
 <p>Sample II $C_{35}H_{26}O_8N_2$</p>	 <p>UVASORB 2 OH (Sigma)</p>	116–120	80
 <p>Sample III $C_{27}H_{44}O_4N_4$</p>	 <p>tetramethyl-piperidinol (Sigma)</p>	151–160	64

$$\ln\left(\beta \frac{d\alpha}{dT}\right) = \ln[Af(\alpha)] - \frac{E}{RT} \quad (2)$$

For $\alpha = \text{const.}$ and using various heating rates, the plot $\ln[\beta(d\alpha/dT)]$ vs. $1/T$ should be linear. From the slope and the intercept of the straight line the value of activation energy (E) and product $[Af(\alpha)]$ were obtained.

The data collected in Table 2 indicate a rather non-uniform variation of E vs. α . Thus, the usage of the activation energy in this case for any considerations and discussions on the thermal stability of the studied compounds is not acceptable.

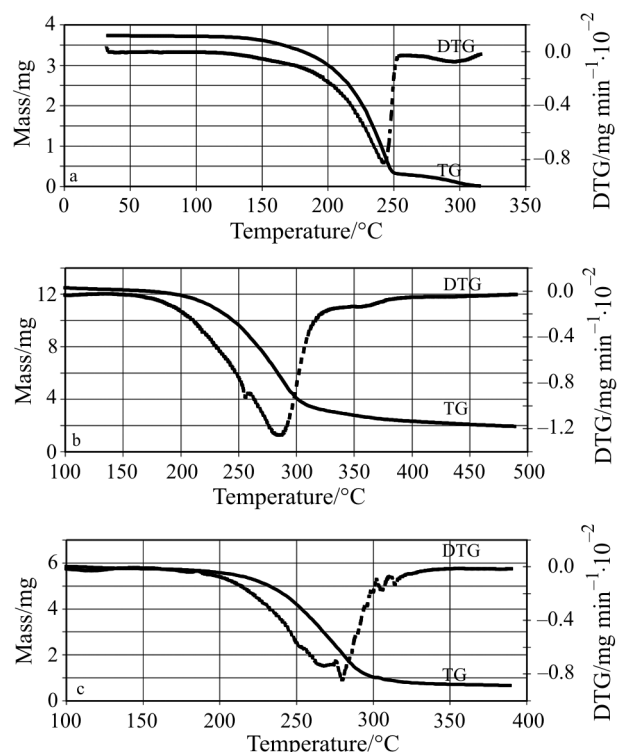


Fig. 1 The TG and DTG curves of the sample at a heating rate of 10 K min^{-1} ; a – sample I, b – sample II and c – sample III

Processing of the TG data by the Budrugeac–Segal method

The procedure is based on the following assumptions [4–6]:

- E and A depend on the degree of conversion and do not depend on the heating rate

- E and A are correlated through the compensation effect (CE)

$$\ln A = aE + b \quad (3)$$

- the dependence of E on the degree of conversion is given by

$$E = E_0 + E_1 \ln(1 - \alpha) \quad (4)$$

where E_0 and E_1 are constants

- the differential conversion function, $f(\alpha)$ has the form

$$f(\alpha) = (1 - \alpha)^n \quad (5)$$

From the differential conversion function (5) it follows that

$$\ln[Af(\alpha)] = \ln A + n \ln(1 - \alpha) \quad (6)$$

and from the values of $[Af(\alpha)]$ and α , the values of $\ln A$ corresponding to various values of n can be obtained. The plot of $\ln A$ vs. E should be linear as required by the existence of compensation effect (Eq. 3). The correct value of n will be that which gives a correlation coefficient closest to 1.00 for the straight line $\ln A$ vs. E .

The presence of the kinetic compensation effect presumes the existence of an isokinetic temperature that can be estimated from the slope of the straight-line $\ln A$ vs. E .

$$T_i = \frac{1}{Ra} \quad (7)$$

From Eqs (1)–(4) we obtain:

$$\ln\left(\beta \frac{d\alpha}{dT}\right) = \left(b + aE_0 - \frac{E_0}{RT}\right) + \left(aE_1 - \frac{E_1}{RT} + n\right) \ln(1 - \alpha) \quad (8)$$

In Fig. 2 the Eq. (8) was simulated using the parameters listed in Table 3 and compared with the experimental points and the agreement is rather good.

It is necessary to mention that a linearity of E vs. $\ln(1 - \alpha)$, in sense of Eq. (4), is observed for: $0.2 \leq \alpha \leq 0.9$ at sample I, $0.3 \leq \alpha \leq 0.9$ at sample II and $0.3 \leq \alpha \leq 0.8$ at sample III.

In Table 4 a comparison between the activation energy E evaluates by Friedman’s method and calculated using Eq. (4) with the data from Table 3 is performed.

Table 2 Activation energy ($E/\text{kJ mol}^{-1}$) obtained by Friedman’s method at a heating rates of 7, 10, 12 and 15 K min^{-1}

Sample	α								
	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
I	74.50±2.9	54.97±2.4	42.21±2.0	36.71±1.6	39.06±1.6	38.58±1.6	38.63±1.6	30.56±2.0	19.80±0.6
II	94.27±1.4	82.63±1.9	96.90±0.5	94.42±1.0	99.74±1.5	95.80±1.5	93.25±1.9	84.71±2.7	62.97±4.3
III	171.9±7.2	55.00±1.6	72.62±1.9	74.40±2.2	79.44±2.3	83.99±2.7	88.43±1.2	77.77±5.3	37.80±4.8

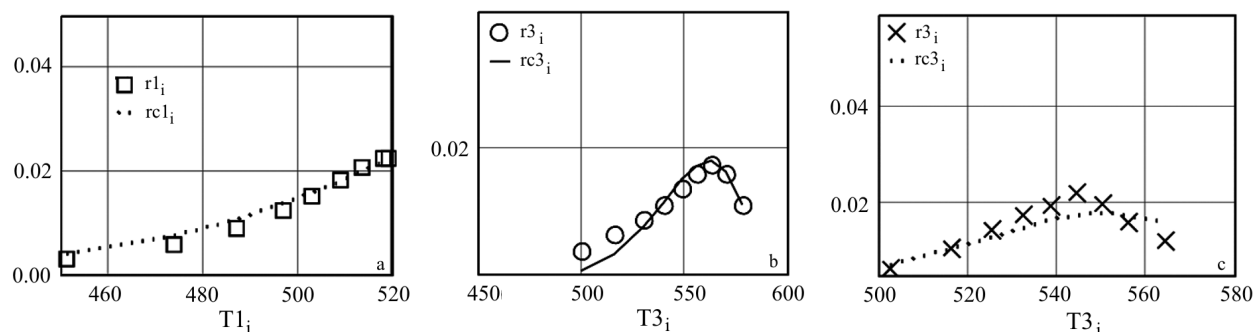


Fig. 2 Experimental (DTG) and simulated (Eq. (8)) reaction rate vs. T at 12 K min^{-1} ; a – sample I, b – sample II and c – sample III

Table 3 Kinetic parameters according to Eq. (8)

Sample	$E_0/\text{kJ mol}^{-1}$ (Eq. (4))	$E_1/\text{kJ mol}^{-1}$ (Eq. (4))	$a \cdot 10^4/\text{mol J}^{-1}$ (Eq. (3))	b (Eq. (3))	n	Corr. coeff.
I	49.93	12.65	2.21	-3.35	0.1	0.99850
II	108.06	16.94	2.09	-2.67	0.8	0.99991
III	73.51	-6.73	2.26	-3.89	0.6	0.99985

The values of the two methods are in a good agreement for α between 0.5 and 0.7. Obvious, the variation of E values is in agreement with Eq. (4).

Processing of the TG data using a modified NPK method

The non-parametric kinetics (NPK) method [7–9] of Serra, Nomen and Sempere is based on the assumption that the reaction rate can be expressed as a product of two independent functions, $g(\alpha)$ and $f(T)$. The reaction model $g(\alpha)$ accounts for the dependence on the conversion degree and $f(T)$ accounts for temperature dependence. The reaction rate $\beta d\alpha/dT$, measured from several experiments at different heating rates, β , was interpolated as a surface in a 3D space ($\beta d\alpha/dT$, α , T). This surface is organized as an $i \times j$ matrix where the rows correspond to different degrees of conversion, from α_1 to α_i and the columns correspond to different temperatures from T_1 to T_j . The i, j element of the matrix A is then $A_{ij} = g(\alpha_i) f(T_j)$. The function $g(\alpha)$ and $f(T)$ can be

discretized and expressed as column vectors, u_0 and v_0 , respectively, where elements are the discretised values of the functions $g(\alpha)$ and $f(T)$.

$$u_0 = \{g(\alpha_1) g(\alpha_2) \dots g(\alpha_i)\} \quad (9)$$

$$v_0 = \{f(T_1) f(T_2) \dots f(T_j)\} \quad (10)$$

The reaction rate can then be expressed in the form of a matrix as:

$$A = u_0 \cdot v_0^T \quad (11)$$

The NPK method uses the singular value decomposition (SVD) algorithm to decompose matrix A into the two vectors u_0 and v_0 . These vectors can be further analyzed by examining the resulting plots of rate vs. α (to determine the kinetic model) and of rate vs. temperature (to determine the Arrhenius parameters). The u_0 vector is given by the first column of the matrix U and v_0 from the first column of the matrix V where:

$$A = U(\text{diag } s)V^T \quad (12)$$

Table 4 Comparison of activation energies (kJ mol^{-1}) at different degrees of conversion obtained by Friedman (FD) and Budrugeac–Segal (BS) methods

Sample		α					
		0.3	0.4	0.5	0.6	0.7	0.8
I	FD	42.21	36.71	39.06	38.58	38.63	30.56
	BS	45.42	43.47	41.16	38.34	34.70	29.57
II	FD	96.90	94.42	99.74	95.80	93.25	84.71
	BS	102.00	99.40	96.30	92.50	87.70	80.80
III	FD	72.62	74.40	79.44	83.99	88.43	77.77
	BS	75.90	76.90	78.20	79.70	81.60	84.30

and s is the vector of singular value.

With the values of α , $\beta(d\alpha/dT)$ and T obtained from TG and DTG data, the surface of the reaction rate in a three-dimensional space (α , T and $\beta(d\alpha/dT)$) was obtained (Fig. 3).

In Fig. 4 the discretized elements of matrix A for sample I is presented.

After the SVD algorithm, the matrix A presents a s vector with two significant values. In this case the matrix A is a sum

$$A=A_1+A_2=u_1 \cdot v_1^T + u_2 \cdot v_2^T \quad (13)$$

It means that there are two elementary processes by the decomposition step and the discrimination between them is possible by the values of the explained variance λ_1 and λ_2 ($\lambda_1 + \lambda_2 \approx 100\%$).

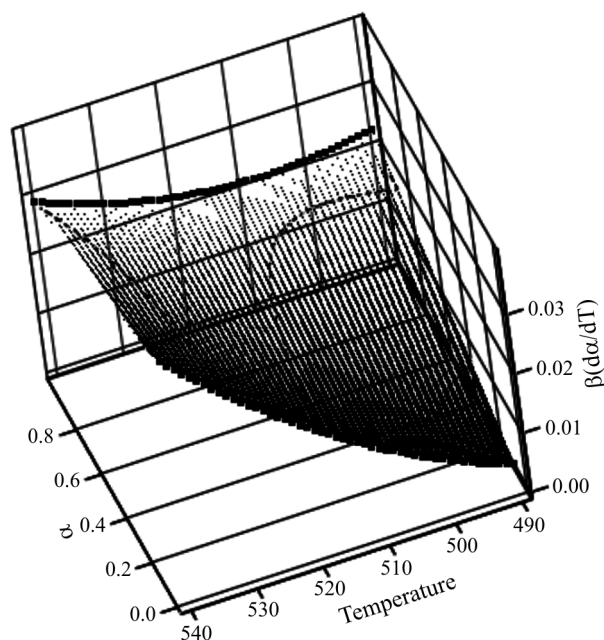


Fig. 3 Surface of reaction rates for sample I generated by multivariate regression

A =	0.00337	0.00277	0.00317	0.00458	0.00700	0.01041	0.01484	0.02026	0.02670
	0.00742	0.00630	0.00619	0.00709	0.00899	0.01189	0.01580	0.02071	0.02662
	0.01142	0.00979	0.00916	0.00954	0.01093	0.01331	0.01670	0.02110	0.02650
	0.01537	0.01323	0.01208	0.01195	0.01281	0.01469	0.01756	0.02144	0.02633
	0.01927	0.01661	0.01495	0.01430	0.01465	0.01601	0.01837	0.02173	0.02610
	0.02312	0.01995	0.01777	0.01660	0.01644	0.01728	0.01912	0.02197	0.02583
	0.02692	0.02323	0.02054	0.01886	0.01818	0.01850	0.01983	0.02216	0.02550
	0.03067	0.02646	0.02326	0.02106	0.01986	0.01967	0.02048	0.02230	0.02512
	0.03437	0.02965	0.02592	0.02321	0.02150	0.02079	0.02109	0.02239	0.02470

Fig. 4 Matrix A obtained by discretization of surface in Fig. 3

The vectors u_1 and u_2 were fitted with a Šesták–Berggen equation [11] (Fig. 5)

$$g(\alpha) = \alpha^m (1-\alpha)^n [-\ln(1-\alpha)]^p \quad (14)$$

and the vectors v_1 and v_2 , with the Arrhenius equation, respectively (Fig. 6).

The results of the kinetic analysis are collected in Table 4.

From the values of the explained variance, it seems that sample I decomposes rather in a single process ($\lambda_2 \approx 10\%$) and this is also in connection with significant lower thermal stability (the lowest value of the activation energy). In comparison, samples II and III present two significant thermal decomposition processes. The superposition of these processes in the TG

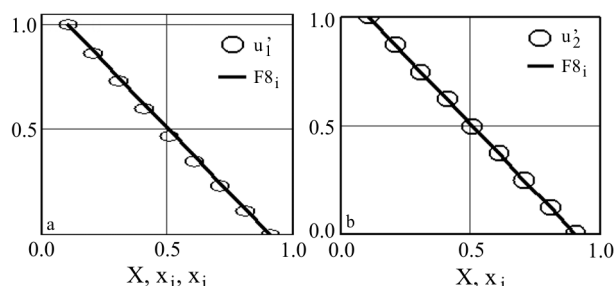


Fig. 5 Simulated and determined values of the normalized vectors u for sample I; a – main process and b – secondary process

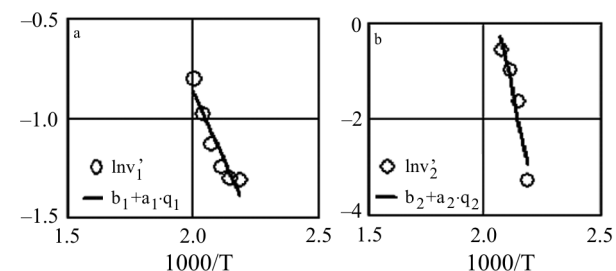


Fig. 6 Linearized Arrhenius equation ($\ln v$ vs. $1/T$); a – main process and b – secondary process

Table 5 Kinetic parameters for the NPK method

Sample		$\lambda/\%$	$E/\text{kJ mol}^{-1}$	A/min^{-1}	n	m	p
main process	I	82.5	25.56	$1.44 \cdot 10^2$	1	–	–
	II	62.8	71.04	$1.78 \cdot 10^6$	1	–	1
	III	57.0	83.32	$3.48 \cdot 10^7$	1	–	1
secondary process	I	17.4	227.2	$2.73 \cdot 10^{22}$	1	–	–
	II	34.4	135.9	$1.15 \cdot 10^{12}$	1	–	–
	III	40.2	79.63	$3.16 \cdot 10^8$	1	–	1/3

curve is obviously kinetically influenced (values of E).

The parameter $n=1$ (Eq. (14) and Table 4) indicate the decomposition of a pure condensed phase in which the reaction occurs homogeneously and without dilution of the reactant by reaction products (mass loss of $\approx 85\%$ on TG curves). This is in agreement with the decomposition after melting of the compounds. The values of $p \neq 0$ are probably due a diffusional contribution to the kinetic law.

Conclusions

- the kinetic of the decomposition under non-isothermal conditions of three bis-urethane was studied. The compounds were prepared by a catalytic addition of hydroxy-compound to toluylene-diisocyanate
- three methods for the kinetic analysis of the TG and DTG data were used. The Friedman's method does not offer certain values for the kinetic analysis. The Budrugaec–Segal method offers an invariant part of the activation energy, but the kinetic description is too formal
- 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 functions of a rate equation

- the decomposition of the urethane in melted state avoid any complication by reactions occurred in solid-state. In this case the kinetic model agrees with a homogeneous decomposition of a pure condensed phase with additional transport

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