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Kinetic analysis of non-isothermal solid-state reactions: multi-stage modeling without assumptions in the reaction mechanism

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A novel non-linear regression method for modeling non-isothermal thermogravimetric data is proposed. Experiments for several heating rates are analyzed simultaneously. The method is applicable to complex multi-stage processes when the number of stages is unknown. Prior knowledge of the type of kinetics is not required. The main idea is a consequent estimation of parameters when the overall model is successively changed from one level of modeling to another. At the first level, the Avrami–Erofeev functions are used. At the second level, the Sestak–Berggren functions are employed with the goal to broaden the overall model. The method is tested using both simulated and real-world data. A comparison of the proposed method with a recently published 'model-free' deconvolution method is presented.

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1. Introduction

In a thermogravimetric (TG) analysis, the response variable, m(t), is a sample mass measured as a function of heating time t. In the case of a non-isothermal (dynamic) TG experiment, the temperature T increases

$$T=T_0+\beta t,$$

at a constant heating rate β . Usually, TG measurements are conducted in a series where each run is performed at a particular heating rate, β_{ν} , $\nu = 1, ..., V$, here *V* is the number of runs.

Thermo-degradation of a solid sample is a complex process that generally involves many stages (steps). To employ a kinetic method of modeling, the raw response *m* is transformed into a variable, α , called the extent of conversion or simply conversion. It is defined as

$$\alpha(t) = \frac{m(0) - m(t)}{m(0) - m(\infty)}.$$
 (1)

The kinetic analysis¹ of the TG data is based on a conventional approach where the total conversion α is presented as a sum of partial conversions α_i ,

$$\alpha = b_1 \alpha_1 + \cdots + b_I \alpha_I, \qquad (2)$$

where b_i is the weighting coefficient that represents the contribution fraction during each stage, and *I* is the number of stages.

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Weights $\mathbf{b} = (b_1, \dots, b_l)$ are naturally constrained: $b_i \ge 0$ and $b_1 + \dots + b_l = 1$.

In general, the kinetics of each single-stage process is presented by the following equation:

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = k_i(T)f_i(\alpha),\tag{3}$$

where k_i is the reaction rate constant, and f_i is the kinetic model of an individual stage. Usually, the function k(T) is described by the Arrhenius model:

$$k(T) = A \exp(-E/RT), \tag{4}$$

where A is the pre-exponential factor, E is the activation energy, and R is the gas constant.

An appropriate kinetic analysis provides for the selection of all unknown parameters that describe the experimental data in the best way. Adopting the least squares approach, in case all kinetic models f_i are known, we arrive at the following optimization problem²

$$\underset{\mathbf{b},\mathbf{A},\mathbf{E}}{\text{minimize}} \sum \left(\alpha_{\text{data}} - \alpha_{\text{model}} \right)^2, \tag{5}$$

where α_{data} is the experimental value given by eqn (1), and α_{model} is the model value calculated using eqn (2)–(4). Optimization is performed with respect to the unknown parameters: preexponential factors A_i , the activation energies E_i , and the stage weightings b_i . Considering that i = 1, ..., I, a total of 3*I* unknown parameters are to be estimated using a non-linear regression (NLR) approach.³

This is a difficult computation task,⁴ which becomes even more challenging in the case where the kinetic models f_i of the

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$$f(\alpha) = q(1 - \alpha)[-\ln(1 - \alpha)]^{1 - 1/q}.$$
 (6)

Other models, *e.g.* the Sestak–Berggren model $(SB)^7$

$$f(\alpha) = \alpha^m (1 - \alpha)^n, \tag{7}$$

have little kinetic meaning, but they facilitate data analysis serving as a kind of 'umbrella' that covers various kinetic functions.⁸ Thus, one can obtain a wide selection of models with different formal properties, varying parameters q in eqn (6), and parameters n and m in eqn (7).

Thinking in an idealistic way, we can imagine a perfect approach to the TG data analysis when all functions in eqn (3) are replaced with the umbrella model given in eqn (7). After that, the optimization problem, presented in eqn (5), is solved regarding the three kinetic vectors (A, E, and b), as well as the two shape vectors (m, and n). Since each of these vectors has a dimensionality of I, a total of 5I unknowns have to be estimated. Unfortunately, this approach cannot be utilized due to various problems. Among them are the computation difficulties, such as the loss of accuracy when solving differential equations, given by eqn (3) and (7). However, the most important is the general problem of multicollinearity. The latter means that the estimates of several unknown parameters (e.g. A and E, and A and b) are found to be highly correlated.^{4,9} In practice, multicollinearity manifests itself as a degradation of the objective function (eqn (5)) when its surface looks like a ravine without an explicit minimum point.¹⁰ Another angle of this phenomenon is the so-called compensation effect,¹¹ which actually has no physical meaning but reflects an imperfect estimation of the Arrhenius parameters, A and E.

There are very few ways to get over multicollinearity. The majority involve a linear regression, *e.g.* principal component analysis and partial least squares. In our opinion, in the case of NLR, the most promising direction is the Bayesian approach¹² when the relevant auxiliary kinetic data are collected and formalized into *a priori* information, which afterwards is added to the objective function given in eqn (5). The authors have not seen publications that discuss and apply this approach, though.

In the literature, several impressive applications^{13–15} of the NLR approach can be found. However, in all cases, the kinetic models have been selected primarily on a know-how basis, or chosen from a list of pre-defined models. Several attempts to develop a general approach based on a generalized logistic function^{16,17} have been criticized¹⁸ as methods that cannot derive kinetic parameters with a clear physical meaning. However, recently, it has been demonstrated^{19,20} that good fitting (with DSC and TG data) can be obtained for each curve separately, in such a way that the fitted parameters are related to the true kinetic parameters.

In chemometrics, methods that utilize substantial physicochemical (mechanistic) assumptions in the modeling are termed as 'hard' (or 'white') models.²¹ In contrast, soft-modeling approaches (a.k.a., 'black' models), like multivariate curve resolution,²² are meant to describe processes without explicitly using the underlying chemical information. Several soft-modeling approaches to the TG data analysis have been recently proposed. All these methods have a common feature. They analyze differential kinetic curves, that is $z = \Delta \alpha / \Delta t$, but not the conversion response, α , itself. Numerical differentiation of integral data tends to magnify noise, but, at the same time, it helps to reveal reaction details.

The "non-parametric kinetics" (NPK) is an innovative approach²³ that makes use of a singular value decomposition²⁴ to represent differential data matrix **z** as the product of two vectors **k** = $k(T_{\nu})$ and **f** = $f(\alpha_j)$ (compare eqn (3)) without any prior knowledge about the kinetic model $f(\alpha)$ and the Arrhenius parameters.

Another soft-modeling method³⁰ employs the empirical SB model, given in eqn (7), to represent a single-stage kinetics. Parameters m and n are obtained from the equation

$$\ln z - n \ln(1 - \alpha) - m \ln(\alpha) = \ln cA - E/RT, \qquad (8)$$

that, in an ideal case, should represent a linear dependence between the left part of eqn (8) and the variable 1/T. To find these values, the authors suggest a rather strange criterion based on the Pearson correlation maximization. In this manner, the slope and intercept of the straight line represent the values of -E/R and $\ln(cA)$, respectively. The application of this method is given in ref. 31.

These methods have a similar disadvantage – they are applicable to single-stage kinetics only. In the case of multistage kinetics, the soft methods do not suggest any clear way for the separation of stages.

A 'model-free' method for the analysis of complex overlapping processes is proposed in ref. 25. This approach implies a successive analysis of the differential profiles z(T). Each profile, obtained at a heating rate β_{ν} , is deconvoluted as a linear combination of suitable peak functions, such as Weibull distribution²⁶ or Fraser–Suzuki.²⁷ Later on, an individual peak (stage) is considered at various heating rates with a goal to calculate the Arrhenius parameters employing some isoconversional method (*e.g.* Friedman²⁸ or Kissinger²⁹). The disadvantage of this approach is the individual deconvolution of each kinetic curve. Therefore, the Arrhenius parameters calculated using this method should be taken with care.

Thus, we can conclude that the considered methods of TG analysis – the idealistic white modeling by NLR and the heuristic black modeling by anamorphosis – are burdened with inherent shortcomings which cannot be improved inside the methods. To surmount these difficulties we have to find a new way that should lie somewhere in between the White Mountain and the Black Forest. This could be a grey method of modeling.^{32,33} This approach aims to develop an empirical model whose parameters have a direct chemical or physical meaning. This is achieved by incorporating known chemical or other knowledge into a model.

In this paper we suggest an example of grey modeling that is applicable to the S-shaped TG curves.

2. Method

The core issue of this approach is the employment of the AE kinetics, given in eqn (6), as a 'small umbrella' model³⁴ for the TG data analysis. The AE kinetics has a unique feature among the popular kinetic models. If $f(\alpha)$ is an AE function, the differential equation eqn (3) has an explicit solution, that is

$$\alpha(t) = 1 - \exp[-p(t)^{q}].$$
 (9)

Here

$$p(t) = A \int_0^t \exp\left(\frac{E/R}{T_0 + \beta\tau}\right) d\tau$$
(10)

is a well-known 'temperature integral'.³⁵ In the literature, there have been many approximations for this function, but we prefer our own that is inspired by the research of S. Seglets.³⁶ We employ the approximation

$$p(x) \approx A \frac{E}{\beta R} x^{-2} \mathrm{e}^{-x} G(x),$$
 (11)

where

$$x = \frac{E/R}{T_0 + \beta t}; \quad G(x) = \frac{0.7284x + 0.2387x^2}{1 + 1.2056x + 0.2387x^2}.$$
 (12)

This approximation provides the relative accuracy not worse then 10^{-4} , for x > 4. A similar approach was used in ref. 37.

In this way we come to a closed-form solution of eqn (2) that can be explicitly calculated in the elementary functions for any given values of predictors: t, β , T_0 , and parameters: A, E, b, and q. The optimization problem, given in eqn (5), becomes relatively simple since it contains no differential or integral equations that should be numerically calculated. The number of stages I is not known in advance, so the TG data analysis is conducted by successively increasing the I values, until the solution becomes acceptable.

The proposed 'grey' approach combines two important advantages. The first one comes from the black side, and it is a fast and stable way of the model computation. The second benefit is from the white side, because the employed models have a clear kinetic meaning, which ensures reasonable estimates of the Arrhenius parameters: *A* and *E*.

The AE kinetics with an additional 'scaling' factor C can be used for the approximation of different models conventionally employed for the TG data analysis. Table 1 demonstrates several examples. For the selection of the optimal parameter q, we used the L₂ norm criterion, that is

$$Q(q) = \|Cf_{AE}(\alpha, q) - f(\alpha)\| / \|f(\alpha)\|,$$
(13)

where $||h||^2 = \int_{0.05}^{0.95} h^2(\alpha) d\alpha$.

At the same time, the SB function multiplied by factor C provides a bigger umbrella that covers even more kinetic models. That is why the proposed 'grey' method can be naturally extended in the following way. Each of the AE kinetics, optimized with respect to eqn (5) along with its estimated parameter q, can be fitted to the scaled SB model. In the result, every stage of the analyzed TG process is presented as a differential equation, eqn (3). In general, the optimization of the multi-stage kinetic data, which stages are given in the form of differential equations, is a difficult computation task. Using the values of the unknown parameters, found in the frame of the AE approach, as an initial guess essentially increases the convergence. An overview of the entire approach is shown in Fig. 1.

Computational aspects

The critical issue for a successful and stable solution of the optimization problem given in eqn (5) is the pertinent transformation of variables and parameters. The objective of this pretreatment is to decrease correlations between the estimates of the model parameters. The main target is the correlation between the estimates of the paired Arrhenius parameters: the activation energy E_i and the corresponding pre-exponential factor A_i ,

$$\rho_i = \operatorname{corr}(\hat{E}_i, \hat{A}_i), \tag{14}$$

where *i* is the stage index. These correlations directly affect the multicollinearity phenomenon – the less correlation, the low the conditional number. The formal definition of the conditional number, N_c , is the ratio of the maximal and minimal eigenvalues of the Hessian matrix calculated for the NLR objective function in the optimal point. The following rule of thumb explains the role of N_c as an important characteristic of an NLR problem.

Suppose that our computer ensures an accuracy of ν decimal digits in conventional arithmetic calculations. In case $N_l = \log_{10}(N_c) = \kappa$, up to κ digits of accuracy would be additionally lost due to numerical methods used in optimization. Therefore, the total assured accuracy is $\nu - \kappa$. In practice, $\kappa > 10$ obstructs

 Table 1
 Kinetic models which can be approximated by the scaled Avrami-Erofeev function

Reaction model	Code	$f(\alpha)$	q	С	Q (%)
First order (Mampel)	F1	$(1 - \alpha)$	1	1	0
Second order	F2	$(1-\alpha)^2$	0.81	0.51	10
Third order	F3	$(1-\alpha)^3$	0.72	0.31	14
Fourth order	P2	$(1-\alpha)^4$	0.66	0.20	16
Phase boundary controlled reaction (contracting area)	R2	$(1 - \alpha)^{1/2}$	1.22	1.55	12
Phase boundary controlled reaction (contracting volume)	R3	$(1 - \alpha)^{2/3}$	1.12	1.32	7
One-dimensional diffusion	D1	$1/2\alpha^{-1}$	0.57	1.11	12
Two-dimensional diffusion	D2	$[\ln(1 - \alpha)]^{-1}$	0.54	1.65	6
Three-dimensional diffusion (Jander)	D3	$3/2(1-\alpha)^{2/3}[1-(1-\alpha)^{1/3}]^{-1}$	0.52	5.69	2
Three-dimensional diffusion (Ginstling-Brounshtein)	D4	$3/[2(1-\alpha)^{-1/3}-1]^{-1}$	0.53	6.76	4
Random scission of polymer chain $L = 2$	L2	$2(\alpha^{1/2} - \alpha)$	1.39	0.91	5



Fig. 1 Summary of a three-level approach for simultaneous fitting of the complex multi-stage TG data.

the solution of a regular NLR problem. In this paper⁴ it has been shown that an appropriate scaling and a tuned re-parameterization can yield an essential reduction in N_c , and, in this way, improve the steadiness of the optimization problem.³

Scaling of the variables aims to make all variables (factors) dimensionless and to be close to 1. For example, time (min) is divided by $\overline{t} = 60$ (min), and temperature (K) is divided by 1000 (K). In this way we obtain the following ranges of the scaled variables: 0 < t < 1, 0.4 < T < 1.2, and $0.4 < \beta < 1.2$. This is an outer type of transformation that directly changes the data.

Reparameterization is an inner type of transformation. It has no influence on the data themselves, but it affects the structure of the reaction model. Consider a stage with index *i*. Let E_i and A_i be the Arrhenius parameters of this stage. We introduce new parameters

$$a_i = \ln(\bar{t}A_i) - \frac{E_i}{R\bar{T}_i}; \quad F_i = \frac{E_i}{\bar{E}_i}, \tag{15}$$

where \overline{E}_i and \overline{T}_i are the 'mean' values of temperature and energy, which are selected for each stage *i* separately, and \overline{t} is the time scaling factor. Using the introduced parameters, the reaction rate constant k_i , given in eqn (4), can be represented as follows:

$$k_i = \exp(a_i - F_i u), \tag{16}$$

where

$$u = \frac{\bar{E}_i}{R} \left(\frac{1}{T} - \frac{1}{\bar{T}_i} \right) \tag{17}$$

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is a 'local reciprocal temperature' valid at stage i.

For model fitting and estimation of unknown parameters we use software FITTER.³ This program utilizes the modified gradient search method with the recurrence algorithm for the inversion of the Hessian matrix.^{38,39} On each iteration, the method provides the conditional number and completeness of search. A distinct feature of FITTER software is the analytical calculation of derivatives, which ensures a high precision of computing.

4. Experiment

For illustration of the proposed method we consider two examples based on both simulated and real-world data.

4.1. Simulated data

The first example is modeled as a two-stage data set simulated for heating rates 5, 10, and 20 °C per minute in the range of 200–900 °C. The stage kinetics are selected from Table 1: the F2 model is used for the first stage, and the R2 model is employed for the second stage. These models are chosen because their approximations by the AE kinetics are not perfect – the relative errors are 10% and 12%, respectively. The parameters used in the simulation are presented in Table 2 (column 'Simulation'). The goal of this experiment is to demonstrate that a complicated procedure of the TG data analysis shown in Fig. 1 – from the AE to SB modeling – is able to restore the initial model. Therefore, we do not disturb the data with errors. The simulated data are shown in Fig. 2 by means of markers.

4.2. Polycarbonate samples

The second example is a real TG experiment with a poly bisphenol A carbonate material. Polycarbonate (PC) is a widely used polymer known for its excellent electrical resistance and thermal stability.

Thin films of PC, 10–20 µm, were prepared as follows. Powder of non-stabilized commercial grade PC (KazanOrgSynthesis, Russia, $M_n = 30\,000$) was dissolved in chloroform. The solution was spread on a polished glass surface. Traces of the solvent were removed by keeping the films in a vacuum chamber at room temperature for 24 hours. The PC films were subjected to TG analysis, which was carried out using a Q-1500D (MOM Budapest, Hungary) derivatograph combined with an Ecochrom (Russia) attachment. The weight loss, m(t), was recorded as a function of temperature and time. Experiments were conducted in air, at constant heating rates of 5, 10, and 20 °C per minute in the temperature range of 200–880 °C. The m(t) data were pretreated using exponential smoothing and transformed into conversion response $\alpha(t)$ using eqn (1).

The pretreated TG data are shown in Fig. 4 by means of markers. It can be seen that the conversion processes at the higher heating rates (10 and 20 $^{\circ}$ C min⁻¹) are not completed. This creates additional difficulties for the TG analysis.

Table 2 The results of the simulated data analysis by means of grey modeling

Parameter	Simulation	Level 1 AE models	Level 2 SB models	Level 3 SB models
RSS	0.000	0.008	0.007	$3 imes 10^{-18}$
$\begin{array}{l} A_1 (s^{-1}) \\ E_1 (kJ \ mol^{-1}) \\ q_1 \\ m_1 \\ m_1 \\ b_1 \end{array}$	$1.33 \times 10^{+5}$ 100.0 2 0 0.7	$egin{aligned} (0.88 \pm 0.39) imes 10^{+5} \ 99.2 \pm 0.16 \ 0.79 \pm 0.01 \ \ \ 0.63 \pm 0.02 \end{aligned}$	$\begin{array}{c} 0.68 \times 10^{+5} \\ 99.2 \\ \\ 1.11 \\ -0.27 \\ 0.63 \end{array}$	$egin{array}{c} (1.33 \pm 0.00) imes 10^{+5} \ 100 \pm 0.00 \ \ 2.0 \pm 0.0 \ 0.0 \pm 0.0 \ 0.7 \pm 0.0 \ \end{array}$
$egin{array}{llllllllllllllllllllllllllllllllllll$	0.23 40.0 0.5 0 0.3	$\begin{array}{c} 0.99 \pm 0.14 \\ 47.28 \pm 0.13 \\ 1.26 \pm 0.05 \\$	1.26 47.28 0.92 0.21 0.37	$\begin{array}{c} 0.23 \pm 0.00 \\ 40.0 \pm 0.00 \\ \\ 0.5 \pm 0.0 \\ 0.0 \pm 0.0 \\ 0.3 \pm 0.0 \end{array}$



Fig. 2 Fitting of the simulated TG data (open markers) with the AE kinetic models (solid curves). Numbers and colors represent the heating rates: 5 (1, blue), 10 (2, green), and 20 °C min⁻¹ (3, red). Contribution of stages is shown by the dashed curves.

5. Results

5.1. Simulated experiment

The simulated data set is analyzed using the proposed method illustrated in Fig. 1. In this particular case, the number of stages, *I*, is known, so iterations at Level 1 are not required. Certainly, in this case, we applied scaling and the re-parameterization procedure explained in Section 3. However, we will not go into such details now, but will return to them in the next subsection, where a case of the real world data is considered. Here, all estimated parameters are shown in Table 2 in their natural units. In the expression $a \pm b$, b means standard deviation. The last three columns demonstrate the results obtained at Levels 1, 2 and 3 as described in Fig. 1.

The first row in Table 2 shows values of the residual sum of squares (RSS) for the objective function introduced in eqn (5). The RSS values correspond to the minimum of the sum of the residuals achieved at the optimal values of the sought parameters. Naturally, the RSS value obtained for the simulation model equals to zero. At Level 1, RSS = 0.008. This reflects the fact that the AE kinetics differ from the models used in the simulation. At the same time, the activation energies and the pre-exponential factors for the AE models are somehow close to the initial values given in column 'Simulation'. Fig. 2 presents the solution found at Level 1. Open markers stand for the TG values $\alpha(T)$ 'acquired' at the heating rates 5 (1, blue),

10 (2, green), and 20 °C min⁻¹ (3, red). The corresponding solid curves demonstrate the obtained AE kinetic models. The dashed curves represent two parallel stages at three heating rates, $b_{\mu,k}(T, \beta_{\nu})$, that is, *i* = 1 and 2, and ν = 1, 2, and 3. The colors of the dashed curves correspond to the colors of the solid curve. This means, for example, that the sum of two blue dashed curves gives the solid blue curve 1.

In line with the procedure shown in Fig. 1 (Level 2), we approximate the found AE kinetics with the determined parameters (rows q_1 and q_2 in column 'Level 1') by the SB models. These approximations are shown in Fig. 3.

The optimization yields the SB model parameters m and n (rows m_1 , n_1 , m_2 , and n_2), and the scaling factors C_1 and C_2 . These factors are used to correct the pre-exponentials A_1 and A_2 , found at Level 1, to be used in the SB models. These corrected parameters are shown in column 'Level 2'. They are used as an initial guess in the final optimization procedure, which is labeled Level 3 in Fig. 1. The final estimates are shown in column 'Level 3' in Table 2. From these results we can conclude that the goal of this example has been achieved – the final model is equivalent to the initial model with high accuracy.



Fig. 3 Simulated data. Fitting of the AF kinetics (markers) with the SB model (curves) at stages 1 and 2.

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5.2. PC thermogravimetry

The second example is analyzed in a similar way. In this case, the number of stages, *I*, is unknown. Therefore, multistage TG models based on the re-parameterized AE kinetics are investigated at the increasing number of stages (Level 1 in Fig. 1). The results are shown in Table 3, which contains the dimensionless parameters explained in Section 3.

The first row in Table 3 shows the RSS values. At I = 3 (three stages), we obtain RSS = 0.01, which seems rather low. To assess this, it is reasonable to compare this result with the corresponding value of 0.02, which has been obtained as the sum of the other squared residuals, $\alpha_{data} - \alpha_{raw}$, where α_{raw} values represent the raw, non-smoothed TG data. We can conclude that the accuracy of the NLR solution obtained for the three-stage AE model is comparable with the experimental error. Therefore, this is the ultimate solution that does not require a more complex description. This solution is shown in Fig. 4. The layout of this plot is similar to Fig. 3 with the difference that in this case we have a three-stage model.

Observing this plot we can understand the role of the third stage in the entire kinetic process. At the heating rate of 10 °C min⁻¹ (green), we have measured only the initial part of the kinetics of the third stage with conversion that is less than a half of the stage equilibrium (green dashed 2-3). At the rate of 20 °C min⁻¹, we had no chance to obtain the data reflecting this stage, because its contribution is smaller than the experimental error. That is why the corresponding red dashed curve 3-3 is completely located on the *T*-axis. This finding is a good affirmation of the power of the proposed method. The third stage was revealed only due to an integral approach to the TG data processing, when all heating rates and all probable stages were analyzed simultaneously using the

 Table 3
 The results of the PC data analysis by means of the re-parameterized

 AE models at the increasing number of stages

Parameter	1 stage	2 stages	3 stages
RSS	1.38	0.09	0.01
<i>a</i> ₁	0.87 ± 0.03	1.4 ± 0.02	1.37 ± 0.01
F_1	0.96 ± 0.08	1.04 ± 0.04	1.01 ± 0.01
q_1	0.87 ± 0.07	1.77 ± 0.07	2.10 ± 0.04
b_1	1	0.63 ± 0.01	0.55 ± 0.00
ρ_1	-0.02	0.09	-0.10
\overline{T}_1	0.715	0.675	0.67
\overline{E}_1	6.0	9.0	9.1
a_2	_	0.08 ± 0.02	0.66 ± 0.04
F_2	_	0.89 ± 0.03	1.01 ± 0.04
q_2	_	2.11 ± 0.14	1.12 ± 0.05
\overline{b}_2	_	0.37 ± 0.01	0.29 ± 0.01
ρ_2	_	0.03	0.06
\overline{T}_2	_	0.73	0.74
\overline{E}_2	—	3.0	5.2
<i>a</i> ₃	_	_	-0.35 ± 0.01
F_3	_	_	1.03 ± 0.06
<i>q</i> ₃	_	_	7.33 ± 0.49
\dot{b}_3	_	_	0.16 ± 0.01
ρ ₃	_	_	-0.05
T_3	_	_	0.66
\overline{E}_3	—	—	1.0
N_l	1	3	5

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Fig. 4 Fitting of the PC TG data (open markers) with the kinetic models (solid curves). Numbers and colors represent the heating rates: 5 (1, blue), 10 (2, green), and 20 °C min⁻¹ (3, red). The contributions of stages are shown by the dashed curves. The third stage is outlined with solid dashes and labeled 1-3, 2-3, and 3-3.

entire kinetic model. There is no doubt that any partial modeling, when the rates and stages are analyzed separately, is not able to find this very hidden stage correctly. We discuss this in detail in Section 6.

From Table 3 we can see that all paired Arrhenius parameters a_i and F_i , given in eqn (15), are close to 1, and their correlations, ρ_i , presented in eqn (14), are rather low. This has been achieved by a proper selection of the scaling values, \overline{E}_i and \overline{T}_i . In the result, we obtain small values of N_i , and an excellent steadiness of the NLR solutions. It should also be noted that when the model complexity, that is the number of stages, is increased, the N_l values also increase. This reflects the loss of precision in computations of the model that is becoming more complex. Scaling of the variables and re-parameterization have a crucial role in compensation for this effect. For example, in case we employ the Arrhenius parameters *A* and *E* in their 'natural' units, which are s⁻¹ and J mol⁻¹, the model manifests the following outcomes: $N_l = 15$, $\rho_1 = 0.999$, $\rho_2 = 0.988$, and $\rho_3 = 0.996$. This implies a high degree of multicollinearity that makes the NLR solution practically unattainable.

The outcomes of the application of the AE kinetics look very promising. Nevertheless, we are going to improve it further using a wider umbrella function, which is the SB model. The procedure is shown in Fig. 1 as Levels 2 and 3. The ultimate results are given in Table 4, the layout of which is similar to the layout of Table 2. In this particular case, we observe no significant improvement in the model fitting, but several kinetic parameters have changed.

6. Discussion

6.1. Kinetics of PC degradation

The results presented in Table 4 can give us some ideas regarding the kinetic mechanism of the thermo-oxidative destruction of PC.

The first stage of this process has a principal practical meaning and therefore it has been studied in numerous publications described in ref. 40. The authors report rather different values of activation energy, and our estimate fits this range very well. It has been shown⁴¹ that the first stage involves oxidative hydrogen cleavage from the isopropylidene linkage followed by a carbon– carbon bond scission. In our model, the stage reaction mechanism is defined by the SB function with parameters: $m_1 = 0.85$ and $n_1 = 0.56$. It can be noted that this function can be fitted using the random scission kinetic model⁴² with L = 2.3. Parameter *L* denotes the minimum length of the polymer that is not volatile.

The second stage is not presented in the literature. We found a trace of this process in a publication,⁴⁰ where the authors noted that after the completion of the main degradation step, the residue continues to degrade in air, eventually going to zero. Considering that the residue remains constant in nitrogen, we can suppose that the kinetics of the second stage is mostly caused by an oxidative degradation of the residues of the first stage. In our model, we obtained the first order kinetics ($m_1 =$ 1.02 and $n_1 = 0.06$) that can be explained by the oxygen excess. The rate of the second stage is rather low, and it is eventually limited with the yield of the first stage residues.

The kinetics of the third stage are absolutely opaque because of the difficulty and complexity of the analysis of the residues involved in this process of degradation. We can only note that the stage activation energy is extremely low, about 4.5 kJ mol⁻¹, and could even be zero. This may be explained by the following considerations. The kinetic rate of the third stage is much higher than the second one. Therefore, the degradation of the residues is much faster than their input, hence the kinetic rate does not depend on the heating rate.

These findings can be collected in the following gross kinetic scheme:

stage 1 PC
$$\xrightarrow{k_1}$$
 R₁ + V₁ L_n random scission
stage 2 R₁ + O₂ $\xrightarrow{k_2}$ R₂ + V₂ first order (18)
stage 3 R₂ $\xrightarrow{k_3}$ V₃ ?

where R_s are non-volatile, and V_s are volatile products.

The PC data were modeled by means of this mechanism in its simplest form: parallel stages, and an easily computable random scission model at L = 2. The result is shown in Fig. 5. The layout of this plot is similar to the plot shown in Fig. 4 with the difference that a time axis is depicted instead of a temperature axis. Due to the usage of the simplified model, the fitting quality is worse, RSS = 0.03, compared to the one at Level 2. where RSS = 0.01. As shown in the last column of Table 4. the first stage activation energy, $E_1 = 88.1 \pm 1.7$ (kJ mol⁻¹), is close to that defined at Level 2. The second stage energy, $E_2 = 98.2 \pm 10.8$ (kJ mol⁻¹), changes materially. The most interesting thing is that the third stage energy is now estimated to be zero, in line with our considerations above. This finding is demonstrated in Fig. 5, where the third stage kinetics - dashed curves labeled as 1-3, 2-3, and 3-3 - are superimposed for all heating rates.

We have achieved the main goal of this paper, which is the demonstration of the abilities of the new method. A further development of the proposed kinetic scheme of PC degradation will be presented in a subsequent work.

6.2. Comparison with an alternative method

To illustrate the advantages of the proposed method, we compare it with an alternative approach presented in ref. 25. As described in the Introduction, the latter method analyzes differential profiles and separates individual stages by a formal peak deconvolution. The application of the Fraser–Suzuki function²⁷ for fitting the individual stages is employed. Each differential TG curve, which corresponds to a particular heating rate, is processed separately. The number of individual stages is defined by an analyst within the possibilities of the data fitting algorithm. This method is further referred to as the disjoint deconvolution. To compare this method with the above presented

Table 4	The results	of the PC data	a analysis by	means of t	the grey r	nodeling
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Parameter	Level 1 AE models	Level 2 SB models	Level 3 SB models
RSS	0.0095	0.0098	0.0091
$A_1 (s^{-1})$	$(0.93 \pm 0.15) \times 10^{+3}$	$(1.21\pm 0.22)\times 10^{+5}$	$(1.33 \pm 0.23) imes 10^{+5}$
E_1 (kJ mol ⁻¹)	76.10 ± 0.88	76.06 ± 0.97	76.18 ± 0.93
q_1	2.10 ± 0.04	_	_
m_1	_	0.79 ± 0.05	0.85 ± 0.05
n_1	—	0.53 ± 0.02	0.56 ± 0.02
b_1	0.55 ± 0.00	0.55 ± 0.00	0.54 ± 0.00
$A_2 (s^{-1})$	37.85 ± 11.31	40.62 ± 13.98	49.40 ± 19.99
E_2 (kJ mol ⁻¹)	43.49 ± 1.77	43.22 ± 2.36	44.54 ± 2.79
q_2	1.12 ± 0.05	_	—
\overline{m}_2	—	0.95 ± 0.09	1.02 ± 0.07
<i>n</i> ₂	_	0.10 ± 0.06	0.06 ± 0.07
b_2	0.29 ± 0.01	0.29 ± 0.01	0.30 ± 0.01
$A_3 (s^{-1})$	$(5.62\pm 0.49)\times 10^{-2}$	$(2.78\pm 0.69)\times 10^{-1}$	$(1.78\pm0.45) imes10^{-1}$
E_3 (kJ mol ⁻¹)	8.57 ± 0.47	5.45 ± 0.81	4.68 ± 0.77
q_3	7.33 ± 0.49	_	—
m_3	—	0.67 ± 0.16	0.33 ± 0.14
<i>n</i> ₃	_	0.88 ± 0.02	0.83 ± 0.03
b_3	0.16 ± 0.01	0.16 ± 0.01	0.16 ± 0.01
N _l	5	6	6



shown in eqn (18) (solid curves). The plot layout is similar to Fig. 4.

grey modeling approach, we also decompose the same data using the individual stages obtained in the previous section. Further this method is referred to as the joint deconvolution.

Both methods are applied to the differential data, that is $z(T) = \Delta \alpha / \Delta t$. Using the established number of stage, I = 3, we fit the data by means of the disjoint deconvolution. This is performed by the minimization of the sum of squared differences between z(T) and the linear combination of the Fraser–Suzuki functions. In the case of the joint method, the deconvolution is obtained directly, using the SB models found in the previous section – see Table 4. The example of deconvolution obtained for the heating rate 5 °C min⁻¹ is shown in Fig. 6.

The plots demonstrate that the disjoint method approximates experimental data more accurately. In fact, here we have RSS = 0.22, *versus* RSS = 1.07 obtained for the joint method. The main discrepancy is seen in the right plot in the area around $\alpha = 0.5$. However, the inconsistency that looks substantial in Fig. 6b can be hardly noticed in Fig. 4, where the integral TG data fitting is presented. This finding is a good illustration of the well-known fact that a good fitting of the differential data does not mean a good fitting in the integral data.

Deconvolution of stages is only a preliminary step, but not the ultimate goal in the considered approach. Applying the Kissinger

I	Disjoint deconvolution	Joint deconvolution
$E_1 (kJ mol^{-1})$ $E_2 (kJ mol^{-1})$ $E_3 (kJ mol^{-1})$	$\begin{array}{c} 102.6 \pm 9.9 \\ 20.2 \pm 11.9 \\ -23.3 \pm 15.6 \end{array}$	84.9 ± 4.4 65.1 ± 14.2 13.7 ± 11.6

method,²⁹ the activation energy E_i for each individual stage is determined.

The results in Table 5 show that a formal but exact approximation of each differential TG curve separately can lead to a poor estimation of the activation energy for individual stages. For example, the E_1 values are rather similar. At the same time, the values for E_2 differ greatly, and the activation energy E_3 found by the disjoint deconvolution is negative. The quality of estimates is rather poor; the standard deviations are about ten times larger than those obtained in the grey modeling. At the same time, the activation energy estimates calculated by the joint deconvolution are in agreement with the corresponding values presented in Table 4. The obtained results show that the disjoint deconvolution of the TG data should be done with care.

7. Conclusions

The distinct feature of the proposed approach is the simultaneous analysis of all TG processes using a general kinetic model that incorporates several individual stages. The number of stages, as well as the share of each individual stage, is determined in the course of data fitting by means of a non-linear regression technique. The Arrhenius parameters for each stage are estimated together for all temperature programs and thus do not contradict each other. The proposed method of re-parameterization and scaling of the variables presents a way to reduce the degree of multicollinearity and increases the stability of fitting.

Computational difficulties related to the non-linear fitting of the multistage data are overcome by the consequent estimation of the unknown parameters, when the overall model is



Fig. 6 Deconvolution of the TG data for the heating rate of 5 °C min⁻¹. Curves 1, 2, and 3 represent stages, curve 4 stands for the sum of the stages, open dots (5) demonstrate data points. The left plot (a) is for the disjoint deconvolution, and the right plot (b) is for the joint deconvolution.

successively changed from one level of modeling to another. At the first level, the application of the explicit expression for the AE kinetic model notably simplifies the calculations. At the second level, the employment of the SB functions broadens the model to allow the inclusion of kinetic reactions that are poorly approximated by the AE functions. The obtained parameters are used as the starting values for the final data fitting of the differential equations. This way of modeling significantly improves convergence of the final procedure.

The TG data are considered in the natural integral form, without numerical differentiation. This helps to avoid additional disturbances in the data. The analysis of the simulated and real world data sets demonstrates the efficiency of the proposed approach in application to a wide range of models with the S-shape kinetics.

The comparison of the results obtained using the proposed method with those yielded using the deconvolution method demonstrates the superiority of the grey modeling approach.

In this work we focused on thermo-gravitational analysis, but the scope of this approach could be extended to more general dynamical problems. For instance, the proposed method can be applied to diffusion in multi-component mixtures,⁴³ where several exponentially decaying kinetics are simultaneously present.

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