

APPLICATION OF A NEW APPROACH FOR INVESTIGATION OF THE KINETICS OF SUBSTANCE DECOMPOSITION BY MEANS OF NON-ISOTHERMAL THERMOGRAVIMETRY

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ABSTRACT

Using thermal analyzer STA 449 F3 Jupiter (NETZSCH – Germany), thermogravimetric curves were obtained at several heating rates to study various decomposition processes: thermal decomposition of poly(ethylene oxide) (PEO) and dehydration of calcium oxalate monohydrate (COM). A new approach was applied in the mathematical processing of the data to calculate the apparent kinetic parameters and the most probable kinetic models of the summary thermochemical reactions. The average activation energy of thermal decomposition of PEO in nitrogen medium was found to be 192.2 kJ/mol at coefficient of correlation $R^2=0.9932$ and most probable rate-determining model obeying the Avrami-Erofeev equation, $g(\alpha) = [-\lg(1-\alpha)]^{3/2}$. For COM dehydration, the average value obtained was $E_a=82.1$ kJ/mol at $R^2=0.9939$ for a kinetic model described by a power function $g(\alpha)=1-(1-\alpha)^{1/2}$. The results obtained by the direct procedure suggested, without approximation, are comparable by value and precision to these obtained by well known methods.

Key words: *non-isothermal thermogravimetry; decomposition kinetics, poly(ethylene oxide); Ca(COO)2.H2O.*

INTRODUCTION

The methods of thermogravimetric analysis (TG) provide useful information on the physicochemical and kinetic parameters of the transformations that substances undergo under isothermal or non-isothermal heating [1-3]. The results obtained are applicable in materials science and the technologies for preparation, exploitation and recycling of various materials: polymers, fuels, raw materials, waste products, etc.

A major part of the studies are related to the kinetics of thermal decomposition, determination of the apparent activation energy – E_a , pre-exponential factor – A in Arrhenius equation and the function type $g(\alpha)$ describing the most probable summary mechanisms of a certain thermochemical reaction. A number of calculation procedures have been suggested for the determination of the kinetic parameters [4-19] but, recently, the methods of non-isothermal thermogravimetry are preferred which are based on several TG curves recorded at different heating rates, the so called isoconversional methods [15-19]. It is generally considered that this softens the dependence of the values obtained on the $g(\alpha)$ function. Despite the convenience and rapidity in data acquisition, the multi-factor experiment under conditions of non-isothermal TG raises certain difficulties in the determination of the kinetic characteristics. A variant of a new, more precise approach has been described and successfully applied by its author (see the report of N.Nedelchev at the same conference) in studies on the kinetics of CaCO_3 . The procedure is based on the decomposition rate date calculated with higher precision from several TG curves and involves elements of the isoconversional analysis.

The aim of the present work is to verify the applicability of a new method for determination of kinetic models and parameters using various processes of thermal decomposition under conditions of non-isothermal TG analysis and compare the results obtained to these obtained using well known methods described in the literature.

Two different by nature objects were chosen for the study, well known and widely used in various fields – poly(ethylene oxide) and $\text{Ca}(\text{COO})_2 \cdot \text{H}_2\text{O}$.

PEO is quite well known crystalline water soluble non-toxic polymer used in pharmaceuticals, textile industry, as a component in nano-composites, solid state batteries, etc. The thermooxidative

decomposition plays an important role in its preparation and application, that is why data on its kinetic parameters is easily available in the literature [20-22]. However, information on the kinetic models of PEO decomposition is scarce [23, 24], and it would have been quite useful for its stabilization and for recycling purposes.

COM is well known as a standard in thermal analysis practice and, besides its other applications, it is often used as a model in kinetic analyses [25]. Here, the process of dehydration was studied, i.e. the first stage of oxalate decomposition in air and the interval of decomposition of PEO in nitrogen medium.

EXPERIMENTAL

Materials and methods

The PEO used was a product of Neochim Co., Dimitrovgrad, with molecular weight 1.8×10^6 determined viscosimetrically in C_6H_6 at $25^\circ C$; melting temperature $70^\circ C$; degree of crystallinity about 92 % determined by DSC at $\Delta H_{100\%} = 196$ J/g [26]. The samples were kept in drying medium and studied in nascent powdery state with average particle size of 0.12 mm. The samples of $Ca(COO)_2 \cdot H_2O$ (puriss. Aldrich) were used after grounding in agate mortar.

Thermogravimetric analysis was performed on a NETZSCH DSC/TG thermal analyzer STA 449 F3 Jupiter, operating in a dynamic mode at a different heating rate in Pt pan with one-hole lid and sample mass $\approx 5 \pm 0.001$ mg. The other conditions were: a) PEO – temperature interval, $20-600^\circ C$; heating rates of 5, 10, 15 and 20 deg/min in nitrogen flow at a rate of 30 ml/min; b) $Ca(COO)_2 \cdot H_2O$ – temperature interval, $20-320^\circ C$; heating rates of 3, 5, 9, 10, 12 and 15 deg/min; in synthetic air flow at a rate of 30 ml/min;

The raw data is converted to ASCII files and kinetic analysis was carried out using an in-house program based on the generalized equation of the kinetic of the solid-state reactions (1) and some equations from the so-called isoconversional calculation procedures.

$$\frac{d\alpha}{dt} = A \exp\left(-\frac{E_a}{RT}\right) f(\alpha) \quad (1)$$

Several isoconversional methods have been widely used [14-19] for identification of the kinetic models and parameters. They involve carrying out a series of experiments at various heating rates (β), followed by selection of data and processing these with the same degree of conversion α . Then, the dependence $\ln v_\alpha / T^l$ is plotted (Fig. 2 and 4). The E_a determined from this dependence (Table 1) is assumed to be less dependent on the $g(\alpha)$ function than the value determined from a single TG curve. Two of the most popular isoconversional methods are described by the following equations:

$$1) \text{ Ozawa- Flynn-Wall (OFW) [18]: } \ln\left(\frac{\beta_j}{T_{\alpha,i}^2}\right) = \ln\left(\frac{AE_\alpha}{g(\alpha_i)R}\right) - \frac{E_\alpha}{RT_{\alpha,i}}; \quad (2)$$

$$2) \text{ Kissinger-Akahira-Sinose (KAS) [17]: } \ln(\beta_j) = \ln\left(\frac{0.0048AE_\alpha}{g(\alpha_i)R}\right) - 1.0518 \frac{E_\alpha}{RT_{\alpha,i}}; \quad (3)$$

The pre-exponential factor A and the most probable mathematical model can be found using the isothermal subsets of the data acquired from the experiments carried out (Tables 1 and 2).

Two approaches are used to improve the precision of conversion rate determination: 1. Use of *two-way filter* for numeric filtering of the experimental degree of conversion α ; 2. *A suitable new approach for the determination of v_α* .

RESULTS AND DISCUSSION

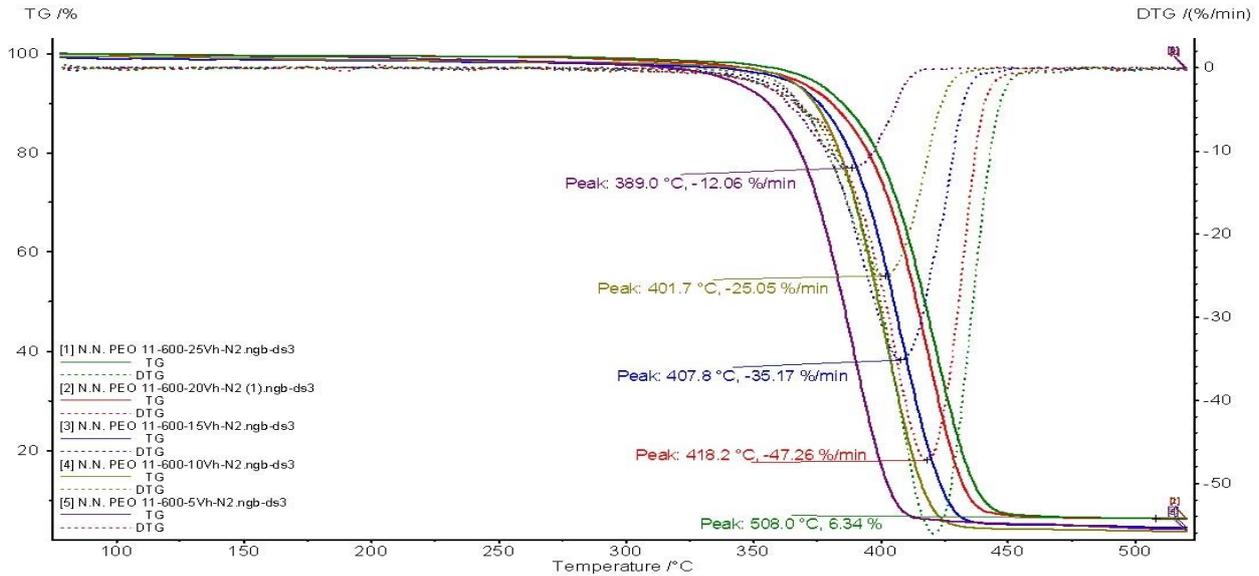


Fig. 1. TG and DTG curves of PEO in nitrogen medium at 5, 10, 15, 20 and 25 deg/min.

It can be seen from the TG curves of PEO taken in nitrogen medium (Fig.1) at heating rates of 5, 10, 15, 20 and 25 deg/min that the beginning of mass loss at a heating rate of 5 deg/min was at about 310°C and shifted to higher temperatures with the increase of heating rate to reach 370°C at 25 deg/min. The decomposition process occurred in one stage which was well illustrated by the single maxima in the DTG curves. The solid residue at 460°C was about 2-3% of sample weight. The values of the rate of a change $-v_a$ and T_a^{-1} were read at 11 selected values of α . From the linear plots $\ln(v_a) / T_a^{-1}$ (Fig.2), the values of the apparent E_a and the coefficient of linear regression R^2 were calculated by the new method (Table 1). In comparison, the values obtained by the methods of Ozawa-Flynn-Wall (OFW) [18] and Kissinger-Akahira-Sinose (KAS) [17] are also given.

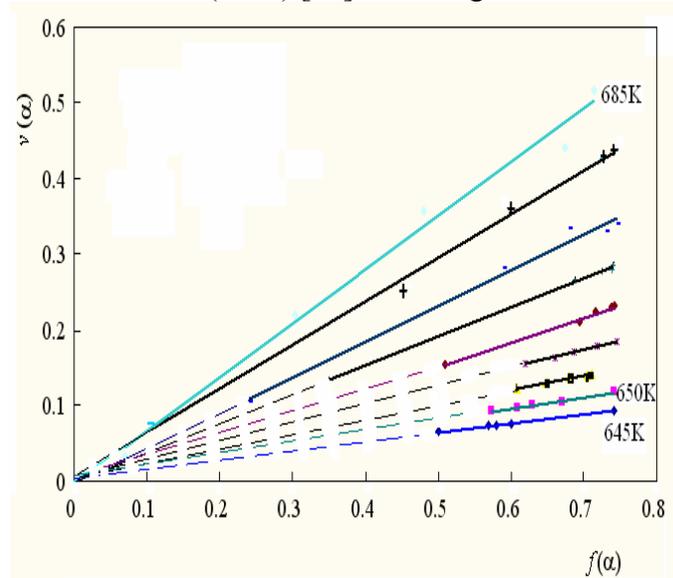
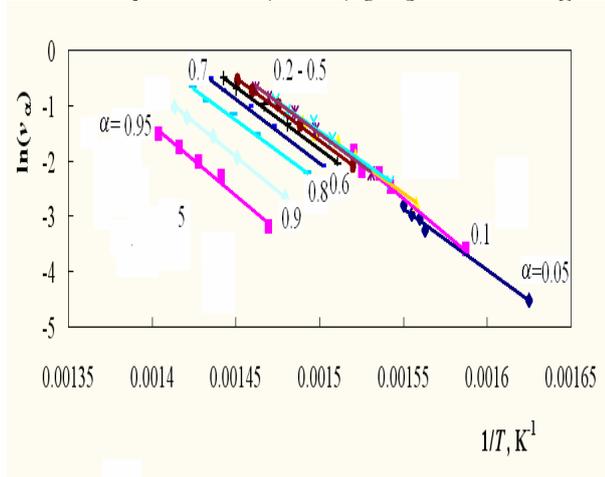


Fig.2. Dependencies of the conversion rate on $1/T, K^{-1}$ at selected values of α .

Fig.3. Dependencies of the conversion rate on the degree of conversion for model $A_{3/2}$

From the 27 decomposition models possible for PEO, $A_{3/2}$ was found to obey the equation of Avrami-Erofeev represented by the function $g(\alpha) = [-\lg(1-\alpha)]^{3/2}$ and corresponds to reaction order of $n = 1.5$.

Table 1. Values of apparent activation energy E_a , kJ/mol for the thermal decomposition of PEO, obtained by different methods at certain degrees of conversion

α	New approach		OFW		KAS	
	E_a	R^2	E_a	R^2	E_a	R^2
0.05	185.1	0.9933	149.1	0.8372	146.3	0.8176
0.1	210.1	0.9833	182.6	0.9378	181.3	0.9310
0.2	179.2	0.9874	188.2	0.9864	187.0	0.9849
0.3	186.8	0.9985	184.6	0.9912	183.1	0.9902
0.4	179.2	0.9946	185.3	0.9945	183.7	0.9938
0.5	188.4	0.9952	185.5	0.9964	183.9	0.996
0.6	188.1	0.9953	185.7	0.9964	184.0	0.9959
0.7	192.9	0.997	185.7	0.9964	186.3	0.9959
0.8	186.1	0.9953	185.46	0.9964	183.8	0.9962
0.9	205.3	0.999	190.6	0.9975	188.9	0.9972
0.95	212.9	0.9861	199.2	0.9961	197.9	0.9956
E_{average}	192.2	0.9932	183.8	0.9751	182.4	0.9722

This mechanism suggests a sigmoidally increasing rate of the summary reactions or generation and growth of nuclei. For the pre-exponential factor A , an average value of 1.168×10^{12} was obtained on the basis of nine isothermal sets between 362 and 412°C. In other studies of PEO in inert media, the values of the activation energy E_a were reported to be from 140 to 200 kJ/mol [22-24]. They are significantly higher than these obtained in oxidative medium [20-22] due to the pronounced affinity of PEO to oxidative destruction – its chemical structure contains oxygen:



The important point here is that the correlation coefficient R^2 , obtained by the approach suggested, is higher than that reported for the other methods, even in the interval $0.1 \geq \alpha \geq 0.9$ where α changes to a smaller extent and the disturbances have the greatest effect.

The first stage of COM thermal decomposition is the release of water molecules in the temperature interval 130-210°C until anhydrous calcium oxalate was obtained and the sample lost 12 mass% of its weight. With the increase of heat rate, it slightly shifted to higher temperatures. The process was registered as a separate step on the TG curve and, respectively, a single maximum on the DTG curve. The procedure used for PEO was applied for each TG curve to obtain the graphical dependencies (Fig.4). E_a and R^2 were determined (Table 2). The average value of the activation energy for model $R_3(F_{1/2})$ was calculated to be $E_a = 82.1$ kJ/mol.

There are a number of publications on the kinetics of COM dehydration and the values obtained by various methods vary from 46 to 100 kJ/mol. The rate-determining mechanisms reported are also different [25]. The values of E_a obtained by the isoconversional method [27, 28] and rate-determining mechanism R_3 corresponding to reactions taking place at the phase border and obeying the equation of shrinking sphere $g(\alpha) = 1 - (1-\alpha)^{1/3}$ were quite close—from 68.7 to 79.0 kJ/mol.

An important issue in the determination of the most suitable model found with the method suggested is that the coefficients of correlation were considerably different for the separate models. The average coefficients of correlation obtained by the new method for the decomposition of PEO were higher than these obtained by the known methods. For COM, they were higher at heating rates up to 10 deg/min.

This was due to the preliminary filtration of the experimental values of sample masses m_i^{exp} and the approach used for the calculation of $v_{\alpha,i}$.

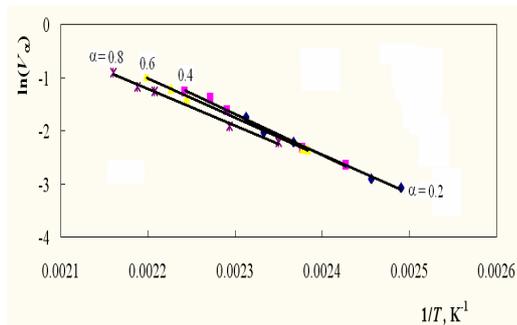


Fig.4. Dependencies of the conversion rate on $1/T, K^{-1}$ for certain isoconversional sets for the process of dehydration of $\text{Ca}(\text{COO})_2 \cdot \text{H}_2\text{O}$.

Table 2. Values of the apparent E_a , frequency factor, A and R^2 obtained for the dehydration of $\text{Ca}(\text{COO})_2 \cdot \text{H}_2\text{O}$

β	A^*	E_a	R^2
deg/min		kJ/mol	
9	$2.27 \cdot 10^9$	84.64	0.9912
10	$1.32 \cdot 10^9$	83.72	0.9905
12	$1.12 \cdot 10^9$	83.27	0.9746
15	$4.29 \cdot 10^9$	79.37	0.9717
20	$6.07 \cdot 10^9$	79.56	0.9644
Average	$1.15 \cdot 10^9$	82.12	0.9785

A^* - for model $R_2 (F_{1/2})$

CONCLUSIONS

1. The thermal decomposition of poly(ethylene oxide) in nitrogen is a single stage process occurring in the range 300-440°C at heating rates from 5 to 25 deg/min without formation of intermediate structures.

2. Using a new approach in the studies on the kinetics of decomposition employing the rate of conversion change instead of conversion itself, as well as precise filtering of the initial TG data, an average value of 192.2 kJ/mol was obtained for E_a of the thermal decomposition of PEO in nitrogen at $R^2=0.9932$ and pre-exponential factor $A=1.17 \times 10^{12}$, with most probable rate-determining model $A_{2/3}$ obeying the Avrami-Erofeev equation $g(\alpha) = [-\lg(1-\alpha)]^{3/2}$.

3. The dehydration of $\text{Ca}(\text{COO})_2 \cdot \text{H}_2\text{O}$ proceeded in a single stage with stoichiometric weight loss ($\approx 12\%$) and under the heating rates used, from 3 to 15 deg/min in the interval 130-210°C.

4. The use of the new approach for the process of COM dehydration gave the following results: average $E_a=82.1$ kJ/mol at $R^2=0.9939$, pre-exponential factor $A=1.15 \times 10^9$ and most probable rate-determining model $R_2 (F_{1/2})$, according to the power equation: $g(\alpha)=1-(1-\alpha)^{1/2}$.

5. The comparative analysis of the results obtained to those reported by us and other authors using the known isoconversional methods showed that the approach suggested is correct and the results are precise enough. The advantage is that the new approach provides possibilities for more accurate determination of the apparent kinetic parameters and more explicit choice of the most probable kinetic model among 27 kinetic equations taken from the literature.

Acknowledgement

The authors are grateful to the fund "Scientific Research", Bulgarian Ministry of Education, Youth and Science for their financial support (project DO-02-61/08).

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