

Effect of poly(ethylene oxide) sample preparation on the results of thermogravimetric analysis

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Aim: To investigate whether the sample preparation process of poly(ethylene oxide) (PEO) affects kinetic analysis of the thermal degradation process. Kinetic analysis was performed to describe the course of a chemical reaction regardless of the reaction conditions and the reaction system complexity. One differential method, the Friedman method, and one integral Kissinger-Akahira-Sunose method (KAS), were applied in this work.

Methods: The PEO sample was prepared in 4 different ways. Thermogravimetric analysis was performed to determine the thermal degradation of prepared samples. Infrared spectroscopic analysis was performed during the preparation of the PEO film obtained by casting from the solution.

Results: Dynamic thermal decomposition of PEO, regardless of the method of preparation, takes place through a single decomposition stage, which is manifested by the appearance of one peak on derivative thermogravimetric (DTG) curve. During the preparation of the PEO film, the procedure was carried out at a temperature higher than its melting temperature ($T_m=65^\circ\text{C}$). After the cooling, the obtained sample didn't solidify and it had an intense odor of acetic acid, which was confirmed by infrared spectroscopic analysis. Samples III and IV were re-prepared at a temperature lower than the melting point of PEO, obtaining samples of satisfactory quality.

Conclusion: In order to prepare poly(ethylene oxide) films by solution casting technique, drying should be carried out at temperatures below the melting point of PEO. If TG analysis of pure PEO powder is compared with the results of hot pressed samples and solution cast samples, it can be concluded that the preparation of the sample doesn't affect the thermal stability of the PEO. The dependence of activation energy calculated by the differential Friedman and integral KAS method on conversion is constant for all samples in a broad conversion range, regardless of how the samples were prepared. The hot pressed samples and solution cast samples have lower activation energy than the commercial PEO powder.

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Introduction

Poly(ethylene oxide) (PEO) is a relatively cheap, conductive, water-soluble and biodegradable polymer. It shows excellent processability, mechanical properties and has a very wide application in various fields of industry. It is used as a component of packaging materials, in the textile industry and coating industry, as a solid electrolyte in batteries, as a material for thermal energy storage and in the manufacture of dosage forms with controlled release of the active substance [1-5]. During their lifetime, polymers are constantly exposed to various loads and interactions with the environment. Their gradual decomposition results in deterioration of many properties from mechanical, chemical, thermal or electrical, to changes in color and appearance [6, 7]. Thermal decomposition research is important for understanding the processing, storage and recovery of polymers, and its possible recycling. Often, the process of thermal decomposition of polymeric materials is investigated by dynamic thermogravimetric analysis. Experimental data collected by this method allow the implementation of kinetic analysis of thermally activated heterogeneous chemical reactions such as polymer degradation. The calculation of the rate and kinetic parameters of the process has a great practical significance, especially for determining the stability of materials in terms of processing and application, as well as in predicting the useful life of products. There are different methods for determining kinetic parameters, but is generally accepted today that for reliable determination of kinetic parameters, it is necessary to accurately determine the dependence of activation energy on conversion [8, 9].

The aim of this work is to investigate whether the preparation of a polymer sample affects the activation energy values calculated on the basis of thermogravimetric analysis data.

Kinetic analysis

Thermal decomposition of polymers in most cases is a complex process, with series of parallel and/or sequential elementary stages, activated by the thermal energy from outside. The aim of kinetic analysis of the thermal decomposition process is to calculate the kinetic parameters of the investigated process and determine their dependence on the process variables. Experimental data required for the kinetic analysis of thermally activated heterogeneous chemical reactions are obtained using thermoanalytical methods such as thermogravimetric analysis (TG), differential scanning calorimetry (DSC) and differential thermal analysis (DTA), under isothermal and dynamic conditions [10]. Since these techniques aren't able to detect elementary reactions and their sequence, but only the total change in the observed physical properties, they don't provide any information about the mechanism of the chemical reaction. Therefore, such techniques are often used in combination with Fourier-transform infrared spectroscopy (FTIR), gas chromatography (GC) and mass spectroscopy (MS), for the analysis of gaseous reaction products, or X-ray diffraction analysis (XRD) and FTIR for analysis of solid reaction products. The kinetic analysis of the experimental data is performed by the kinetic equation for one-step reactions, which is defined as the product of two functions. One depends on the temperature and the other on the degree of conversion [8-12]:

$$r = \frac{d\alpha}{dt} = k(T) \cdot f(\alpha) \quad (1)$$

where r is the reaction rate (min^{-1}), $k(T)$ is constant of the reaction rate (min^{-1}), $f(\alpha)$ is the analytical form of the function of degree of conversion, T the absolute temperature (K), t is the time (min) and α is the conversion. For TG measurements, conversion is defined as the ratio of mass losses at any given time and total mass loss for a given stage of the decomposition process:

$$\alpha = \frac{m_0 - m}{m_0 - m_f} \quad (2)$$

where m is mass of the sample at the time t , m_0 is the initial mass of the sample and m_f is the final mass of the sample. It is assumed that the constant of the reaction rate follows the dependence of Arrhenius equation:

$$k(T) = A \cdot \exp\left(-\frac{E}{RT}\right) \quad (3)$$

where A is the pre-exponential factor (min^{-1}), E is the activation energy (Jmol^{-1}) and R is the general gas constant ($8.314\ 459\ 8\ \text{JK}^{-1}\text{mol}^{-1}$). It is necessary to emphasize that thermal degradation of polymers is a heterogeneous process in which a set of chemical reactions and physical processes proceed with an overall rate. For that reason, the experimentally determined kinetic parameters are called the apparent activation energy and apparent pre-exponential factor.

By including equation (3) in equation (1), the general kinetic equation is obtained [8-12]:

$$\frac{d\alpha}{dt} = A \cdot \exp\left(-\frac{E}{RT}\right) \cdot f(\alpha) \quad (4)$$

This equation describes the total process, and its application assumes that the calculated values of E , A and $f(\alpha)$, i.e. the so-called “kinetic triplet” can describe the overall course of a process regardless of its complexity. Dynamic TG analysis is performed at a constant heating rate $\beta=dT/dt$, where the general kinetic equation (4) takes the form:

$$\frac{d\alpha}{dt} = \beta \frac{d\alpha}{dT} = A \cdot \exp\left(-\frac{E}{RT}\right) \cdot f(\alpha) \quad (5)$$

In integrated form, this equation as follows:

$$g(\alpha) = \int_0^\alpha \frac{d\alpha}{f(\alpha)} = \frac{A}{\beta} \int_0^T \exp\left(-\frac{E}{RT}\right) dT \quad (6)$$

Today is generally accepted that for reliable determination of kinetic parameters, it is necessary to record at least three experimental TG curves at different heating rates and to determine the dependence of activation energy value on conversion using isoconversional methods. Isoconversional methods, also called model-free methods, enable reliable calculation of activation energy without assuming a model $f(\alpha)$. The best known linear integral isoconversional methods are the Flynn-Wall-Ozawa (FWO) and modified Kissinger-Akahira-Sunose (KAS) method [12, 13], whilst the most known linear differential isoconversional method is that of Friedman (FR) [2, 8, 14, 15].

The Flynn-Wall-Ozawa and Kissinger-Akahira-Sunose methods are based on these equations:

$$\log \beta = \log \frac{AE}{Rg(\alpha)} - 2,315 - 0,4567 \cdot \frac{E}{RT} \quad (7)$$

$$\ln \frac{\beta}{T^2} = \ln \frac{AR}{Eg(\alpha)} - \frac{E}{RT} \quad (8)$$

Drawing the dependence of $\log \beta$, i.e. $\ln (\beta/T^2)$ versus $1/T$ for each $\alpha = \text{const.}$ and by applying linear regression analysis, a series of isoconversional straight lines are obtained, from whose slope the activation energy for a certain conversion is determined [2, 6, 13].

Friedman method is based on equation:

$$\ln \left[\beta \frac{d\alpha}{dT} \right] = \ln \frac{d\alpha}{dt} = \ln A + \ln f(\alpha) - \frac{E}{RT} \quad (9)$$

Also, drawing the dependence $\ln [\beta da/dT]$ versus $1/T$ for each $\alpha = \text{const.}$ and applying linear regression analysis, a series of isoconversional straight lines are obtained, from whose slope the activation energy for a certain conversion is determined [2, 8, 15]. The dependence of the activation energy on the conversion provides an insight into the complexity of thermal decomposition process of polymers. If the activation energy doesn't change with the conversion, it can be concluded that it is a simple one-step process. On the other hand, the change in activation energy is indication of the complex, multi-step mechanism of the investigated process.

Materials and methods

Materials

In this work PEO powder, molecular weight $M_w = 300\,000$, Polyox™ WSR N750, manufactured by The Dow Chemical Company, Midland, USA, was used. Distilled water and ethanol mixtures were used as solvent. A sample of pure PEO powder was marked as Sample I.

Preparation of the sample by hot pressing

PEO films with thickness of 0.0576 mm were made using a hand hydraulic press Dynisco LME 230, manufactured by Specac. The polymer powder was pressed for 45 seconds at a pressure of 50.99 Nmm⁻² at temperature of 120°C, and is marked as Sample II (**Figure 1a**).

Preparation of the sample in the form of a film by solution casting

An initial 4% solution of PEO was obtained by dissolving 4 g of PEO in 100 mL of an ethanol/distilled water solvent mixture. Three solutions with different solvent ratios were prepared:

- ethanol : distilled water = 70:30
- ethanol : distilled water = 50:50
- ethanol : distilled water = 30:70.

The weighed powder was transferred to a volumetric flask, covered with a portion of the solvent and left overnight to allow sufficient time for the swelling process. After that, the rest of the solvent was added and the dissolution process was carried out by heating in a water bath ($T \approx 50^\circ\text{C}$). The volumetric flasks were cooled and refilled to the mark. Content of each flask was individually transferred to a round bottom flask connected to a water cooler and heated up to 70°C with reflux and constant stirring for 2 hours. Obtained milky white solutions were casted into Petri dishes. Then, samples were dried at 40°C for 1 day, at 50°C for 1 day and then in a vacuum dryer at 70°C for 3 days. After drying at a temperature higher than the melting temperature of PEO, a wet film of milky white color and odor of acetic acid were obtained. The sample didn't solidify after cooling. Since no films of adequate quality were obtained in the previously described process, solution was prepared by dissolving 4 g of PEO powder in 100 mL of distilled water. Content of the flask was transferred to an Erlenmeyer flask with a ground stopper, sealed and heated to 70°C with stirring for 2 hours. Obtained milky white solution was casted into two Petri dishes. One part of the sample was dried for 1 day at 40°C, 1 day at 50°C (Sample III), while the other part of the sample was additionally dried for 3 days in a vacuum dryer (Sample IV). Drying at a temperature lower than the melting temperature of PEO allowed us to obtain clear and compact films of satisfactory quality (**Figure 1c**).

Methods

Thermogravimetric analysis was used to determine the thermal degradation temperature of the polymer. It was performed using a Perkin-Elmer Pyris 1 TGA thermogravimetric analysis apparatus. Samples weighed approximately 10 ± 0.5 mg. The weight loss percentage of the sample was monitored in a temperature range from 50°C to 550°C, at four heating rates ($\beta = 2.5; 5; 10$ and 20°Cmin^{-1}). Nitrogen gas of ultrahigh purity (20 mLmin^{-1}) was used as the purging gas for the furnace chamber. Infrared spectroscopic analysis was performed using a Perkin Elmer Spectrum One spectrophotometer by the Horizontal Attenuated Total Reflectance (HATR) technique on a flat crystal of zinc selenide (ZnSe, angle of incidence 45°), in the wavelength range 4000-650 cm^{-1} . Signals were collected in

10 scans at a spectral resolution of 4 cm^{-1} and rationed against a background spectrum recorded from the empty ZnSe crystal at room temperature.

Results and discussion

Sample preparation and FT-IR spectroscopy

Sample I was analyzed in pure powder form as supplied by the manufacturer. The hot pressing process yielded a clear and compact film of satisfactory quality (**Figure 1a**), designated as Sample II. Special attention was given to obtaining the film by casting it out of solution. After casting and drying at the temperature higher than the melting temperature of PEO, a wet film of milky white color and odor of acetic acid was obtained which, after cooling, didn't solidify and remained in the form of a viscous gel (**Figure 1b**). An intense odor on acetic acid led to the assumption that a chemical change of the polymer occurred during drying above the melting point.

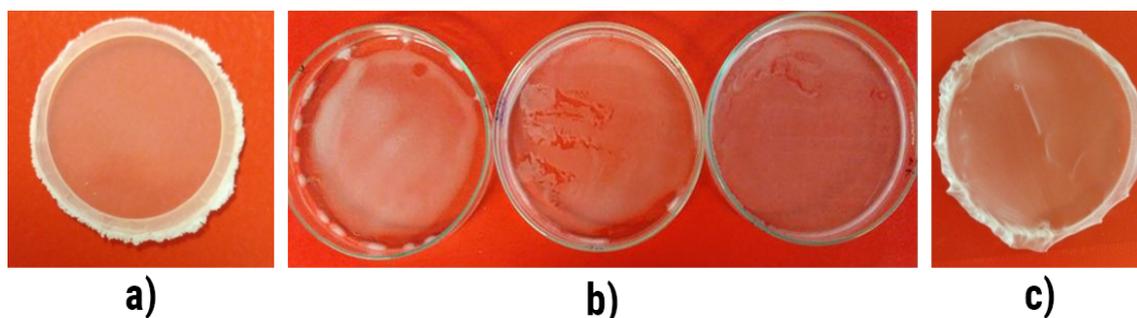


Figure 1. a) Sample II hot pressed film b) Casted film dried at a temperature higher than the melting point of poly(ethylene oxide) c) Casted film dried at a temperature lower than the melting point of poly(ethylene oxide).

To confirm this assumption, FT-IR spectroscopy analysis was performed. **Figure 2** shows the spectrum of Sample I and casted film dried at a temperature higher than the melting point of PEO.

FTIR spectrum

The most significant changes in the absorption band of the PEO powder sample were identified in the wavelength range $2500\text{--}3000\text{ cm}^{-1}$ and in the range $800\text{--}1500\text{ cm}^{-1}$. According to the data in the literature [16], the bands at the wave number 840 cm^{-1} are attributed to the oscillating vibrations of the CH_2 group and the shear deformation (scissors) of the C-O-C group. Symmetrical and asymmetric oscillating vibration and tensile vibration of the CH_2 group, and stretching of the C-C bond, are found at 960 and 945 cm^{-1} . At 1145 , 1093 and 1060 cm^{-1} is the so-called triplet, referring to the symmetrical stretching of the C-O-C group, indicating the existence of a crystalline phase of PEO. The oscillating vibration of the CH_2 group at 1360 and 1341 cm^{-1} represents the so-called “doublet” characteristic of PEO, and the bands at 1466 and 1456 cm^{-1} refer to the asymmetric and symmetric shear deformation of the CH_2 group. Asymmetric and symmetrical stretching of the CH_2 group at 2881 cm^{-1} is represented by a pronounced band. On the FT-IR spectrum of the sample dried above

the melting point (Figure 2), smaller shifts of the characteristic peaks in relation to the spectrum of pure PEO powder are observed. In addition, a wide elongation band of the hydroxyl OH group at a wavelength of 3446 cm^{-1} , a CH bond in the CH_3 group at 2874 cm^{-1} and a C=O elongation at 1720 cm^{-1} are clearly visible, confirming the suspicion that a chemical change occurred in the sample or acetic acid was formed. Acetic acid could be formed by the ethanol oxidation of residual from the solvent, and also from ethanol formed as a product of the thermal decomposition of PEO. Since the polymer film couldn't be obtained in this way, the procedure was repeated with 4% concentrated solutions of PEO in water. Film samples were obtained by casting from the solution whereby Sample III was dried without application of vacuum at a temperature below the melting point of PEO. Sample IV was also dried at the same temperature but additionally under vacuum. The films prepared in this way were of satisfactory quality.

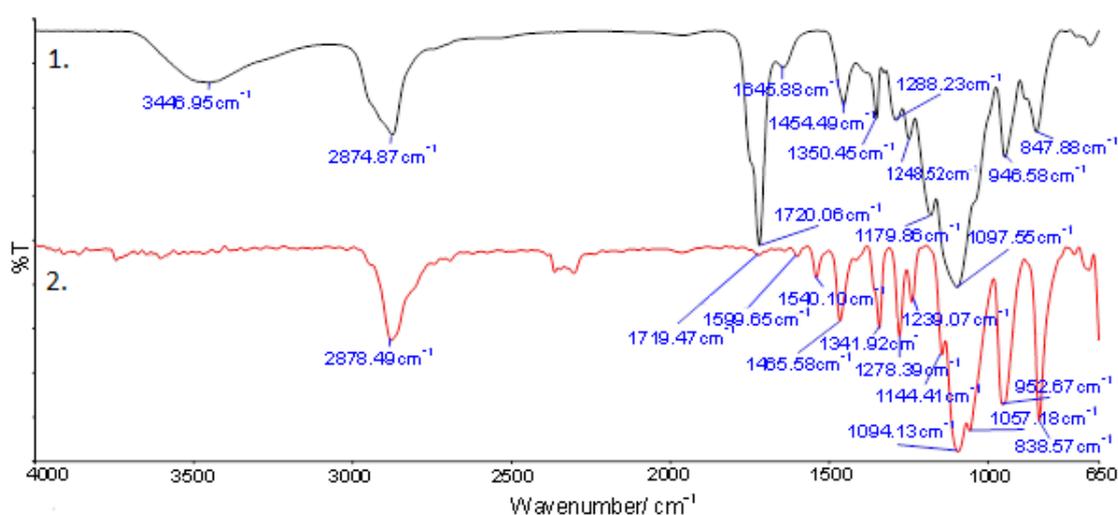


Figure 2. Comparison of FT-IR spectrum of casted film sample dried at a temperature higher than the melting point of poly(ethylene oxide) (1.) and spectrum of pure powder of poly(ethylene oxide)(2.).

Thermogravimetric analysis

The thermal decomposition of the prepared PEO samples was investigated by dynamic thermogravimetry. The result of this analysis are TG and DTG curves of dynamic thermal decomposition of PEO samples, which represent the mass loss, i.e. the rate of mass loss as a function of temperature. Obtained results are shown in Figure 3a-d.

From the shape of the TG and DTG curves, it is obvious that the thermal decomposition of all four PEO samples took place through one stage at all heating rates in the temperature range $330\text{--}450^\circ\text{C}$. Products of thermal decomposition of PEO are low molecular weight compounds: ethanol, methanol, alkenes, non-cyclic ethers (ethoxy methane, ethoxy ethane, methoxy methane), formaldehyde, ethylene oxide, water, CO and CO_2 [16]. When increasing the heating rate, TG and DTG curves shift to higher temperatures and the decomposition rate also increases. Characteristics of the TG and DTG curves are shown in Table 1.

It is common for the thermal stability of polymers to be estimated from the characteristics of TG curves recorded at the lowest heating rate. Decomposition of PEO powder begins at

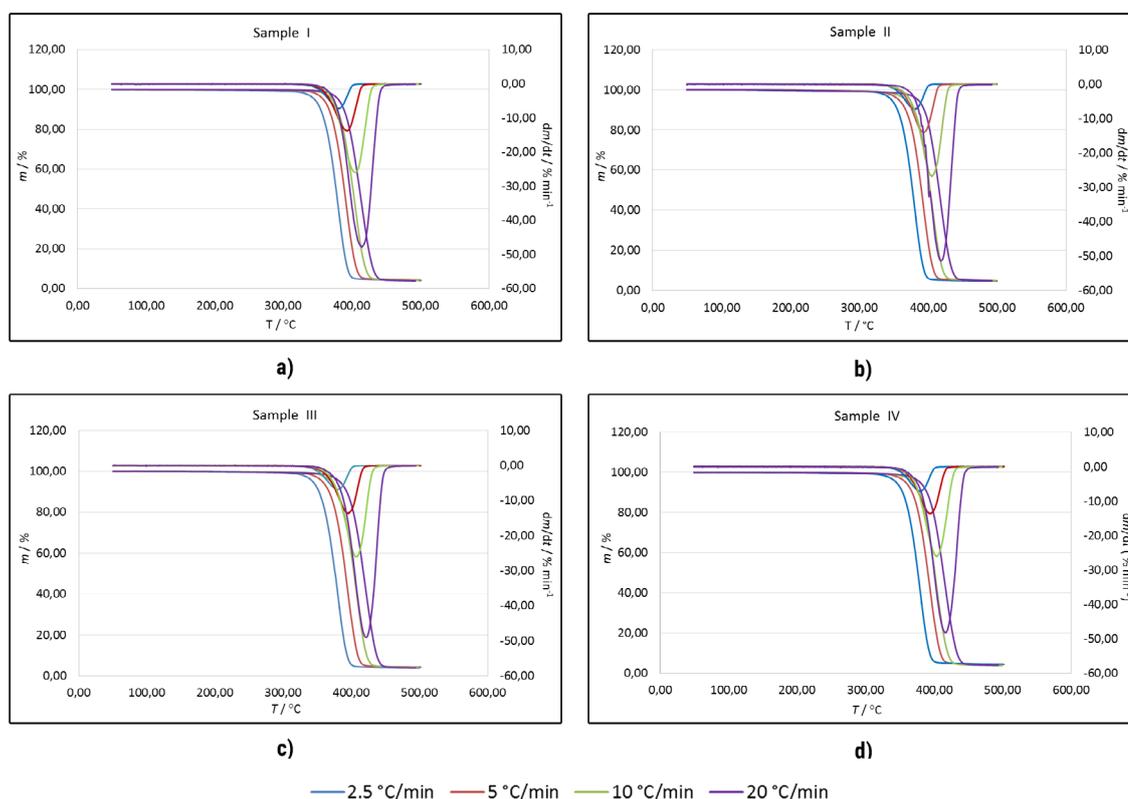


Figure 3. TG and DTG curves of dynamic decomposition at different heating rates for Sample I (a), Sample II (b), Sample III (c), and Sample IV (d).

Table 1. Characteristic of the thermal decomposition process

$^*B / ^\circ\text{C min}^{-1}$	Sample	$^{\dagger}T^0 / ^\circ\text{C}$	$^{\ddagger}T_{5\%} / ^\circ\text{C}$	$^{\S}T_{\text{max}} / ^\circ\text{C}$	$^*R_{\text{max}} / \% \text{min}^{-1}$	$\ \Delta m$	$^{**}m_f / \%$
2.5	I	357	346	380	7.25	95.8	4.2
	II	358	347	380	7.26	95.4	4.6
	III	356	343	380	6.85	96.1	3.9
	IV	358	345	380	7.13	95.7	4.3
5	I	371	359	393	13.75	95.7	4.3
	II	372	357	394	14.11	95.2	4.8
	III	373	357	395	13.62	95.7	4.3
	IV	372	359	394	13.61	95.7	4.3
10	I	383	371	405	25.92	95.8	4.2
	II	385	368	405	26.69	95.1	4.9
	III	383	370	407	25.99	95.8	4.2
	IV	382	369	404	26.17	96.3	3.7
20	I	390	380	415	47.66	96.0	3.9
	II	397	385	419	51.38	95.2	4.8
	III	398	383	422	49.01	96.1	3.9
	IV	393	380	417	48.30	96.2	3.8

*B = heating rate, $^\circ\text{C min}^{-1}$.

$^{\dagger}T^0$ = initial decomposition temperature, $^\circ\text{C}$.

$^{\ddagger}T_{5\%}$ = temperature at weight loss of 5%, $^\circ\text{C}$.

$^{\S}T_{\text{max}}$ = maximum decomposition temperature, $^\circ\text{C}$.

$^*R_{\text{max}}$ = maximum decomposition rate, $\% \text{min}^{-1}$.

$\|\Delta m$ = sample mass change.

$^{**}m_f$ = residual mass of the sample, $\%$.

a temperature of 357°C, and 5% of the total mass is lost at 346°C. The highest degradation rate of 7.25 %min⁻¹ is achieved at 380°C. At temperatures above 450°C, only 4.2% of the initial mass sample remains. Comparing these values with the values for samples II-IV, it can be concluded that the sample preparation doesn't affect the results of thermogravimetric analysis, i.e. the thermal stability of PEO.

Kinetic analysis

The kinetic analysis of degradation process is based on experimental TG curves (Figure 3a-d), from which the temperatures needed to reach each degree of conversion were read off. The analysis begins by determining the activation energy using isoconversional kinetic analysis methods that don't require the assumption of function of degree of conversion $f(\alpha)$, but require recording TG curves at different heating rates and allow the determination of the functional dependence E of α . One differential method, the Friedman method, and one integral Kissinger-Akahira-Sunose method, were applied in this work. Friedman's method is based on equation (9) which is linearized in the coordinate system of the dependence $\ln da/dt$ versus $1/T$ for each $\alpha = \text{const}$. By applying linear regression analysis, a series of isoconversional lines were obtained from whose slope (E/R) the activation energy for a given conversion was calculated. An example of the data display is showed on Figure 4 for Sample I.

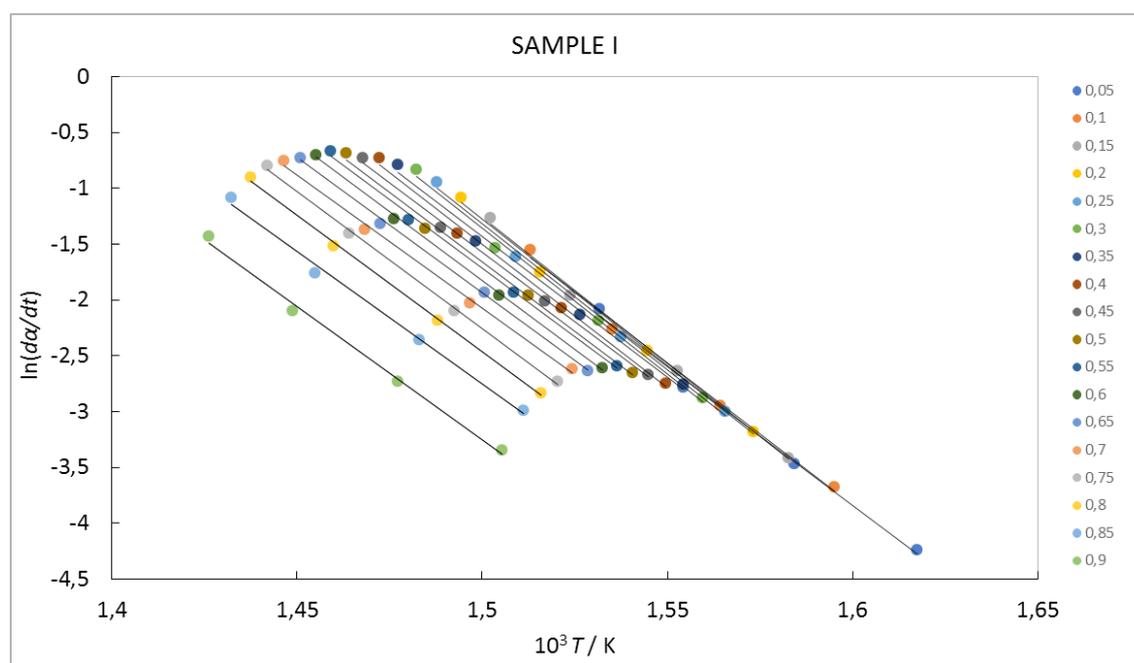


Figure 4. Isoconversional lines series obtained of by Friedman method in representation dependence of $\ln da/dt$ versus $1/T$ for each $\alpha = \text{const}$.

Activation energy values at given conversions of the thermal decomposition process for all four tested samples calculated by the Friedman method are shown in Figure 5.

The average values of activation energy and standard deviation, as well as the difference between the maximum (E_{max}) and minimum (E_{min}) values of activation energy in the conversion range 0.05-0.95, are listed in Table 2. According to the recommendations for per-

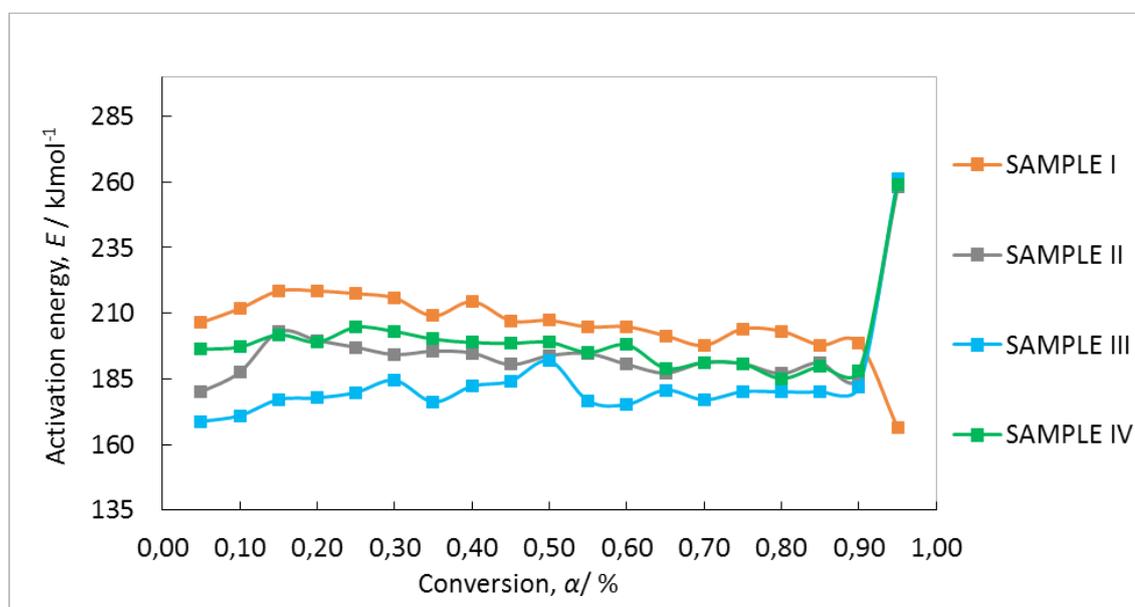


Figure 5. Activation energy values at given conversions of the thermal decomposition process for all four tested samples calculated by the Friedman method.

forming kinetic analysis [8], the dependence of activation energy on conversion can be considered constant if the difference between the maximum and minimum value of E is less than 20% of the mean value of activation energy in the selected conversion area.

Table 2. Average values of activation energy and standard deviation, and the difference between the highest and lowest values of E calculated by the Friedman method for all four samples

Sample	$E_{\text{mean}} (\alpha = 0.05 - 0.95) / \text{kJ mol}^{-1}$	$E_{\text{max}} - E_{\text{min}}$	$0.2 \cdot E_{\text{mean}} - (E_{\text{max}} - E_{\text{min}})$
I	206 ± 12	21	20
II	195 ± 16	23	16
III	184 ± 19	23	14
IV	199 ± 15	74	-34

This condition is met by samples I-III for the conversion range 0.05-0.95; while sample IV satisfies in the conversion range 0.05-0.90. If E changes significantly with α , the process is characterized as kinetically complex, and the form of the dependence E on α helps to determine the kinetic scheme of the examined process.

The Kissinger-Akahira-Sunose (KAS) method is based on equation (8) which is linearized in the coordinate system of the dependence $\ln(\beta/T^2)$ versus $1/T$ for each $\alpha = \text{const}$. By applying linear regression analysis, a series of isoconversional straight lines were obtained, from which the slope (E/R) of the activation energy for a certain conversion was calculated (Figure 6).

The values of activation energy at the given conversions of the thermal decomposition process for all four tested samples calculated by the KAS method are shown in Figure 7.

The average values of activation energy and standard deviation, as well as the difference between the highest (E_{max}) and minimum (E_{min}) values of activation energy in the conver-

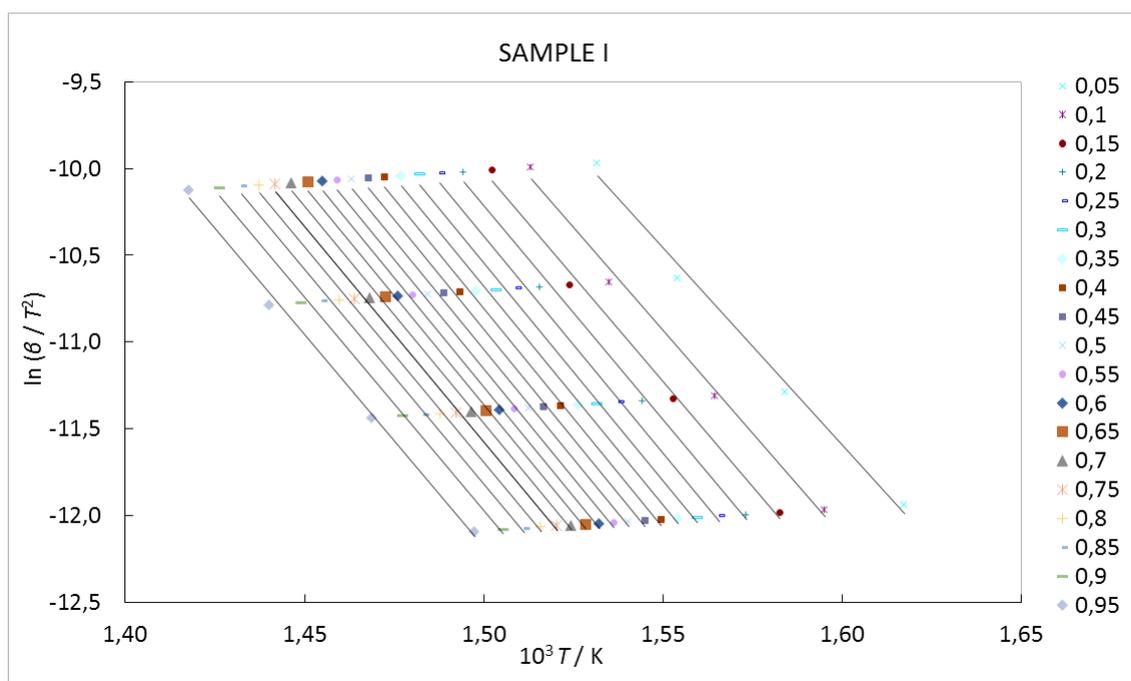


Figure 6. Isoconversional lines series obtained by KAS method in representation dependence of $\ln(\beta/T^2)$ versus $1/T$ for each $\alpha = \text{const}$.

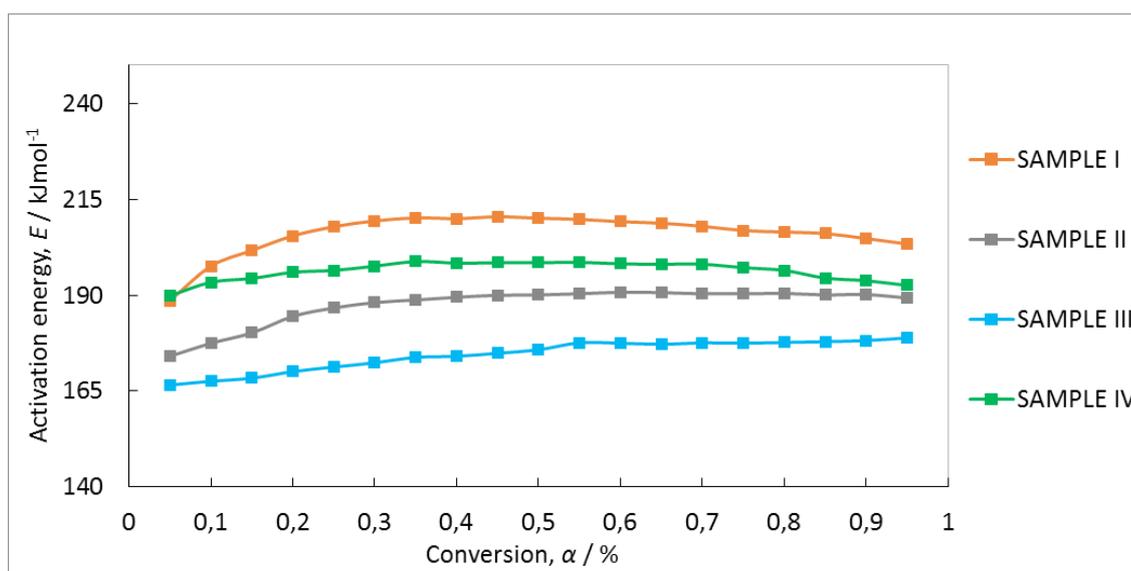


Figure 7. Activation energy at the given conversions of the thermal decomposition process for all four tested samples calculated by the KAS method.

sion range 0.05-0.95 are listed in [Table 3](#). Activation energy values calculated by the KAS method can be considered constant in the conversion range 0.05-0.95 for all samples, since

Table 3. Average values of activation energy and standard deviation, and the difference between the maximum and minimum values of E calculated by the KAS method for all four samples

Sample	$E_{\text{mean}} (\alpha = 0.05 - 0.95) / \text{kJ mol}^{-1}$	$E_{\text{max}} - E_{\text{min}}$	$0.2 \cdot E_{\text{mean}} - (E_{\text{max}} - E_{\text{min}})$
I	206 ± 5	22	19
II	187 ± 5	17	21
III	174 ± 4	12	23
IV	196 ± 3	9	31

the difference between the maximum and minimum value of E is less than 20% of the main value of activation energy in the selected conversion range.

By comparing the values of activation energy of thermal decomposition (E) calculated by the differential Friedman method and the integral KAS method, it can be seen that the integral method gives slightly lower values of the activation energy of the samples obtained by hot pressing and casting out of solution. Also, the E calculated by this method has a smaller deviation from the mean values. The E values of pure PEO powder are higher than the activation energy values of PEO films prepared by hot pressing or casting out of solution.

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