

# POLIMERY

## Study on thermal stability and degradation kinetics of bio-based low-density polyethylene\*

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**Abstract:** The degradation kinetics of low-density bio-based polyethylene three grades were examined using the TGA method in nitrogen and air atmosphere. An analysis of gases produced during thermal decomposition in air was also performed. The mechanism of thermal degradation processes of bio-based polyethylene was proposed in relation to literature data on the thermal decomposition of polyethylene of petrochemical origin.

**Keywords:** bio-based polyethylene, thermal stability, degradation kinetics.

### Badanie stabilności termicznej i kinetyki degradacji biopolietylenu o małej gęstości

**Streszczenie:** Metodą TGA w środowisku obojętnym i utleniającym zbadano kinetykę degradacji trzech odmian biopolietylenu małej gęstości. Dokonano również analizy gazów powstających podczas rozkładu termicznego w powietrzu. Zaproponowano mechanizm procesów termicznej degradacji biopolietylenu w odniesieniu do danych literaturowych dotyczących rozkładu termicznego polietylenu pochodzenia petrochemicznego.

**Słowa kluczowe:** biopochodny polietylen, stabilność termiczna, kinetyka degradacji.

Over 50 years, polyethylene (PE) remains the most processed polymer globally. Its total European market share in 2022 amounted to 24%, translating into the total production of low-density (LDPE) and high-density (HDPE)

varieties at 13.7 Mt/year [1]. It is a non-biodegradable polymer of petrochemical origin; therefore, in many sectors of the economy, attempts have been made to replace it with biodegradable equivalents. However, due to the low cost and excellent properties of polyolefins, exceptionally high durability, chemical resistance, and good processability, the prospect of its replacement by biodegradable equivalents is still distant. An alternative solution to increase the sustainability of polyethylene is the industrial synthesis of bio-based varieties of both HDPE and LDPE, developed in recent years. Using a plant component in the manufacturing process allowed for a significant reduction in the carbon footprint of the final product. Moreover, bio-based polyethylene, according to the categorization discussed by Siracusa and Blanco [2] refer-

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ring to [3] due to the use of starring monomers obtained from renewable resources may be named as bioplastics.

While the production process of bio-based ethylene had its beginnings at the beginning of the 20<sup>th</sup> century, and the first industrial attempts were made already in the 80s, it was only in 2010 that Braskem introduced on a large scale different types of HDPE and LDPE, based only on ethylene of plant origin [4]. Further development of this product meant that its planned production for 2030 would amount to 260 kT/year [5]. Bio-based polyethylene synthesis is a polymerization of ethylene monomer by dehydration of bioethanol from glucose, which can be derived from feedstock like sugar cane, sugar beet, and starch crops [2]. Their phenomenal properties, outstanding fossil-derived PE, and much lower greenhouse gas emissions are characteristic of 'green' grades of PE [6]. Benavides and co-workers [6] compare life cycle greenhouse gas emissions (GHC) and fossil- and bio-derived polyethylene energy use. Significantly lower life cycle GHC emission for bio-based PE was noted as the most significant benefit. The result of this analysis was explained by cancellation by biogenic carbon absorption during biomass growth of CO<sub>2</sub> emission during production and conversion. Moreover, fossil energy consumption (FEC) in the whole life cycle of bioPE was more than two times lower than for petroleum-based grades. Due to the same synthesis and processing methods, processing and manufacturing contribute similarly to the overall FEC, bioPE was characterized by a five times lower share of feedstock.

While the manufacturer and some scientific works suggest no structural and processing differences between bio- and petroleum-based grades of polyethylene [7, 8] using bio-based polyolefins still raises many reservations and concerns among industrial recipients. It should be emphasized that assuming the same chemical structure of polyethylene obtained from components of plant origin, few studies focus on comparing the properties of this polymer concerning the substrates used. Pandey et al. [9] studied the properties of composites based on petroleum and bio-based high-density polyethylene filled with fibers from distiller's dried grain with solubles (DDSG) and corn grain. Despite using bioPE with a lower melt flow index than petroleum grade, the composites produced had better mechanical properties and lower water absorption. This suggests the possibility of success of replacing the petrochemical polymer with a bio-derivative variant. In so far published results, the most considerable number of studies on bio-based polyethylene (bioPE) applications concerns the production of polymer composites, those containing natural fillers in their composition [9-12].

The thermal properties of petrochemical PE grades are described in detail in the literature [13-15], but there are no reports of research on determining these properties for bioPE. The article analyzed the thermal properties, including the kinetics of the degradation process of three

grades of bio-based low-density polyethylene (bioLDPE) and analysis of decomposition products, which allowed the identification of differences between bioLDPE with different structures.

## EXPERIMENTAL PART

### Materials and sample preparation

Three grades of bioLDPE with the trade name LDPE SBC 818 I'm Green<sup>®</sup>, LDPE SEB 853 I'm Green<sup>®</sup> and LDPE SPB 681 I'm Green<sup>®</sup> with a density of 0.918 g/cm<sup>3</sup>, 0.923 g/cm<sup>3</sup> and 0.922 g/cm<sup>3</sup>, respectively, were supplied by Braskem (Brazil). Before testing, the samples were dried at 50°C for 24 hours using a vacuum dryer. Then they were compression molded at temperature of 160°C and pressure of 180 MPa for 2 minutes using a Remiplast laboratory hydraulic press (Poland). After forming, the samples with a diameter of 25 mm and a thickness of 1 mm were removed from between the heated plates, loaded and cooled with forced air flow for 5 minutes. Samples prepared in this way were subjected to thermal degradation tests.

### Methods

#### TGA

Thermogravimetric analysis was performed using Netzsch TG 209 F1 Libra (Selb, Germany) apparatus. The 10 mg samples in Al<sub>2</sub>O<sub>3</sub> crucibles were heated from 20°C to 900°C at a heating rate of 2.5, 5, 7.5°C/min and in an airflow of 40 mL/min. To perform kinetic analysis, the data from a test in the presence of air and nitrogen was used. Test in atmosphere of nitrogen was held by placing the 10 mg samples in Al<sub>2</sub>O<sub>3</sub> crucibles and then heated from 20°C to 900°C at the rates 2.5, 5, 10 and 20°C/min in nitrogen flow 20 mL/min. This data was used to calculate the thermal degradation activation energy. The kinetics of polymer degradation can be described using a kinetic equation:

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

where  $k(T)$  is a rate constant,  $\alpha$  is the conversion of weight loss data, and  $f(\alpha)$  is a conversion function (reaction model). The value of  $\alpha$  is obtained from TGA measurements using the equation (2), where  $W_0$  is the weight of the sample at  $t=0$ ,  $W$  is the weight at  $t=t$ , and  $W_\infty$  is the final weight of the sample.

$$\alpha = \frac{W_0 - W}{W_0 - W_\infty} \quad (2)$$

The function  $k(T)$  represents a temperature-dependent relationship described by the Arrhenius equation:

$$k(T) = Ae^{\frac{-Ea}{RT}} \quad (3)$$

Combining equations (1) and (3) results in:

$$\frac{d\alpha}{dt} = Ae^{\frac{-E_a}{RT}} f(\alpha) \quad (4)$$

where  $E_a$  is the activation energy,  $A$  is the preexponential factor, and  $R$  is a gas constant. To determine the activation energy, researchers employed isoconversional methods. These methods offer a significant benefit in allowing the prediction of kinetic parameters without necessitating the fitting of any specific reaction model. These methods are defined by the principle that when conversion is held constant, the reaction rate becomes a function of temperature [16]. One such method is the Kissinger method [17], which utilizes the Kissinger equation (5). This equation assumes that the reaction rate attains its maximum value at the temperature peak ( $T_p$ ) observed in DTG curves conducted under various heating rates ( $\beta$ ). Notably, the degree of conversion ( $\alpha$ ) at  $T_p$  remains consistent throughout.

$$\ln\left(\frac{\beta}{T_p^2}\right) = -\frac{E_a}{RT_p} + \ln\left(\frac{AR}{E_a}\right) \quad (5)$$

The slope of the straight line from plot  $\ln(\beta/T_p^2)$  vs.  $1/T_p$  (6) is used to calculate activation energy.

$$\frac{d\left(\ln\frac{\beta}{T_p^2}\right)}{d\left(\frac{1}{T_p}\right)} = -\frac{E_a}{R} \quad (6)$$

Another method to calculate the activation energy is the Ozawa-Flynn-Wall method [18, 19]. This method is based on an equation (7).

$$\ln\beta = -1.0516\frac{E}{RT} + const \quad (7)$$

The slope of the  $\ln\beta$  vs.  $1/T$  plot corresponds to the value of  $-1.0516 E/R$ . This relationship is instrumental in the computation of activation energy. Both the Kissinger method and the Ozawa-Flynn-Wall method were applied to ascertain the activation energy associated with the decomposition of bio-polyethylene in a nitrogen atmosphere.

To determine the activation energy in the presence of air, the model-based method was used. The four-step chain reaction is defined as a polyethylene degradation process in air for LDPE SBC 818 and LDPE SEB 853, but LDPE SPB 681 was fragmented into six step degradation reaction. The  $n^{\text{th}}$ -order kinetic model was applied.

$$f(\alpha) = (1 - \alpha)^n \quad (8)$$

The activation energies were calculated for each step using the Netzsch Kinetics Neo software, and the model fit is specified at the level minimum  $R^2=0.99$ .

## TGA-FTIR

The evaluation of gaseous product emissions during the thermal decomposition of the polyethylene grades was carried out in TGA Q500 from TA Instruments (Waters Corporation, Milford, USA) coupled with FTIR Nicolet 6700 spectrometer from Thermo Scientific (Waltham, USA). Samples of about 10 mg were heated in the air from ambient temperature to 800°C at a rate of 5°C/min. The gas flow rate was 10 mL/min in the chamber and 90 ml/min in the oven. The FTIR gas cell was held at 240°C, and the temperature of the transfer line was set to 250°C to reduce the possibility of evolved products condensing along the transfer line. The analyses were performed in a spectral range of 400–4000  $\text{cm}^{-1}$  and with a resolution of 4  $\text{cm}^{-1}$ , using 64 counts.

## RESULTS AND DISCUSSION

According to the literature, thermal degradation of polyethylene in the presence of air is divided into four main stages. The TG measurement in the air atmosphere allows to investigate if degradation of bio-based PE occurs under the same conditions. The experimentally obtained data from thermogravimetric measurements in the air atmosphere of bioLDPE is presented in Figure 1. The course of TG and DTG curves shown in Figure 1 are heterogeneous; this means that there is more than one inflection point, also reflected in DTG peaks. There can be distinguished four DTG peaks for LDPE SBC 818 and LDPE SEB 853 and six for LDPE SPB 681. The initial stage of thermal degradation of polyethylene in oxygen occurs in the amorphous regions of the polymer, resulting in the generation of peroxide radicals. According to the study based on the degradation of petrochemical polyethylene in the air [20], this step starts at 220°C and finishes at 252°C [21]. In this study, the first stages of mass loss begin at 280°C and complete around 350°C or 380°C. The second stage of degradation is also focused on the production of peroxide radicals, the removal of low-molecular products unrelated to the polymer chain, and the degradation of hydroperoxides. The literature indicates that this step is typically within 250 to 340°C [20]. However, it is noteworthy that for all variations of bioPE, this range has been slightly shifted towards elevated temperatures. For LDPE SBC 818, the beginning of this step is around 380°C and finishes at 410°C; a slightly wider range is for LDPE SEB 853 (350–410°C). This is the widest temperature range in the polyethylene degradation process, accompanied by the most significant mass loss. The observed phenomenon is the point at which the literature data diverges from the experimentally obtained results. The degradation of bio-polyethylene LDPE SPB 681 has a six-step degradation; the second peak on DTG curve is placed between 350–370°C, which suggests the additional reaction to the named first in which different reaction products are

Table 1. TGA and DTG data

LDPE grade	$T_{5\%}$ , °C	$T_{max}$ , °C	DTG, %/min
SBC 818	317.1	348.9	-1.79
		377.1	-8.43
		435.3	-5.97
		500.8	-0.51
SEB 853	314,8	370.5	-4.07
		401.6	-7.58
		415.6	-6.78
		506.0	-0.5
SPB 681	305.9	334.6	-2.52
		366.2	-3.02
		385.7	-7.29
		410.6	-4.16
		448.5	-3.55
		508.3	-0.59

formed, and then the second step occurs at 370 to 400°C. The third step usually occurs at the maximum of DTG, which is 410°C and leads to the first chain scission reactions where the C-C chain breaks and macroradicals are formed. Therefore, the chain crosslinking is noticeable, creating a branched structure. During this stage, char develops, restricting oxygen transport to the polyethylene surface. As a result, the formation of peroxides is also constrained, leading to a deceleration in oxidation reactions and promoting chain branching and crosslinking. This third step is recognizable for bioLDPE at 410–460°C, but again, in the DTG of LDPE SPB 681 two peaks are formed, one with the maximum at 410.6°C and another at

448.5°C. This also implies that different degradation products are formed. The last step consists of the reactions which lead to polymer chain termination. The possible termination reactions usually occur at DTG maximum of 460°C. The last step of thermal oxidation of bioLDPEs begins at 460°C and ends at 560°C. Literature explanation suggests that the peak above 500°C is related to the evaporation of low volatile oxidation products [20]. The imputation that this peak in bioLDPEs DTG curves is responsible for chain termination as well as the evaporation of low-molecular-weight volatile compounds will be confirmed or unconfirmed by the kinetic analysis, especially the activation energy and react order analysis.

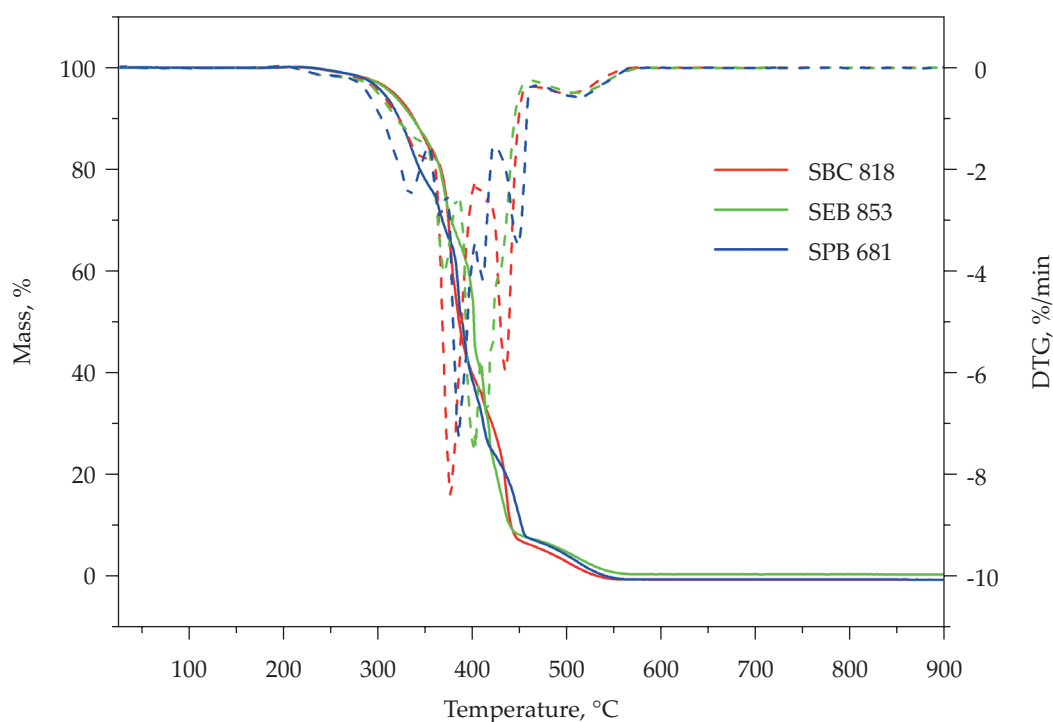


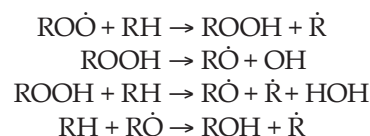
Fig. 1. TG and DTG curves of bio-based polyethylene in air atmosphere



The exact values of the maximum for DTG peaks are collected in Table 1. The value of  $T_{5\%}$  temperature is the lowest for the LDPE SPB 681, which means that the degradation in the air starts for this sample faster. The  $T_{5\%}$  is the value of temperature, where the mass loss is 5%. As previously stated, the four DTG peaks appear for LDPE SBC 818 and LDPE SEB 853, which can be interpreted as maximums for four steps in polyethylene degradation. The location of these peaks is similar for LDPE SBC 818 and LDPE SEB 853. Only the first three peaks are slightly moved towards higher temperatures; to be exact, this temperature is moved by approximately 20°C. The uncharacteristic behavior is observed for air degradation of LDPE SPB 681, where the six peaks in DTG curve are visible. The statement that polyethylene degradation is a four-step process was presented by Tugov and Kostyrykina [21], and experimentally proved by Bolbukh et al. [20]. In their work, the four different steps were obtained by deconvolution DTG peak [20]. In our study, the peaks in DTG graph are clearly visible, without the necessity of deconvolution procedure application.

Another method to investigate the degradation process of polymer materials is to calculate the activation energy. The model-based method was implemented to achieve the activation energies at every degradation step. The experimentally calculated reaction orders ( $n$ ) are presented in Table 2, as well as the activation energies ( $E_a$ ) for each step. The model-free methods are unsuitable for calculating activation energies in this case because of the different courses of thermal degradation among the same sample investigated at different heating rates. Some of the steps may not be visible in higher heating rates because of the overlapping DTG peaks like in the research mentioned above [20], the deconvolution is necessary to highlight them. The course of degradation of LDPE samples was divided into the number of steps obtained in TG measurement at 5°C/min. The activation energies at the first step in thermo-oxidative degradation are similar for every bio-polyethylene, and they have the same high percent of contribution, approximately 50%, which means that half of the degradation processes occur in the first step. The activation energy at this step is about 150 kJ/mol and suggests that the  $\beta$  C-H bond scission occurs to form propyl radicals [21]. According to Peterson, the activation energies in the first step should

be between 80–110 kJ/mol, which consists 40% of the reaction [22]. This activation energy is responsible for peroxide formation in the propagation step and is characteristic of oxygen-initiated depolymerization reaction. The value of this energy is consistent with the energy of peroxides decomposition [23]. The higher activation energy indicates not only the peroxy-radicals formation but also the reaction of these peroxides with the polymer chain to form propyl radicals like in these reactions.



**Scheme 1.** Formation of radicals during PE thermo-oxidative degradation

The next step in thermo-oxidative degradation of LDPE SBC 818 and LDPE SEB 853 has much higher activation energies, above 250 kJ/mol. The activation energies for breaking the bond between carbon and carbon can achieve such high values because the bond dissociation energies for C-C is 248–368 kJ/mol, 615 kJ/mol for C=C, and 812 kJ/mol for C≡C [24]. At this step, the breakage of the polymer chain occurs. The literature shows that further peroxide formation is associated with removing low-molecular products, and ketone formation occurs in the second step. In the third step, the chain cleavage can be observed. This effect aligns with the temperatures at which detailed steps appear; the DTG max is 410°C, according to Bolbukh *et al.* [20]. The previous explanation that the degradation steps for these two bio-polyethylene grades are shifted into the higher temperature can be wrong after analyzing the activation energies. Now, it can be stated that the first two steps of degradation are combined in one stage, and the second step in oxidative degradation of bio-polyethylene is the third step. However, the activation energies at a maximum of 409°C is 69.6 kJ/mol from research conducted by Bolbukh et al. [20] which is not compatible with the activation energies obtained at the second step for bio-based LDPE SBC 818 and LDPE SEB 853. Activation energy obtained by Bolbukh et al. refers to the decomposition of hydroperoxides and reactions of peroxides and alkoxy radicals,

**Table 2.** Kinetic parameters obtained for bioLDPE degraded in air atmosphere

Step No.	SBC 818			SEB 853			SPB 681		
	$E_a$ kJ/mol	$n$	Contrib. %	$E_a$ kJ/mol	$n$	Contrib. %	$E_a$ kJ/mol	$n$	Contrib. %
1.	151.00	1.61	50	141.86	1.54	50.3	146.17	1.69	53.3
2.	272.49	1.80	24.7	256.41	1.63	25.2	151.04	1.41	21.3
3.	116.78	0.51	12.5	106.26	0.53	12	94.05	0.77	7.4
4.	85.06	2.83	12.8	91.50	3.85	12.5	56.21	0.66	8.9
5.	–	–	–	–	–	–	79.45	0.08	4.4
6.	–	–	–	–	–	–	84.54	0.14	4.7

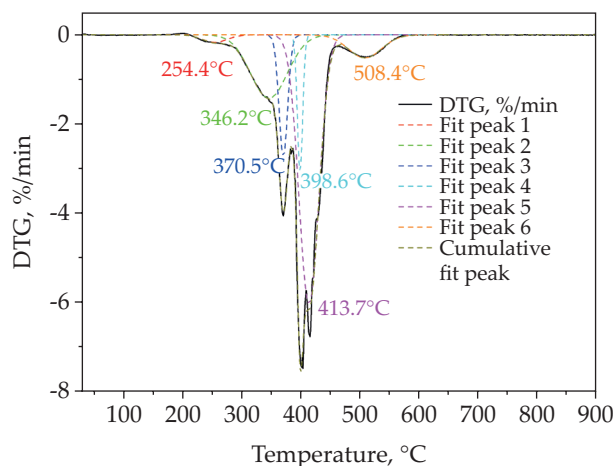
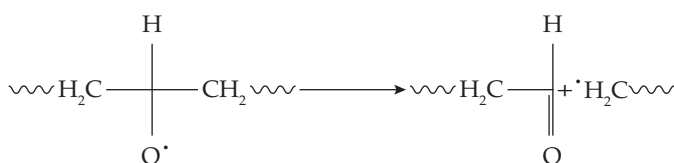


Fig. 2. The deconvolution of DTG peaks for LDPE SEB 853

which can also appear at this step with the chain scission [25]. The mechanism of thermo-oxidative degradation of petrochemical polyethylene and bio-based cannot be easily linked together. The steps defined by the thermogravimetric measurement and activation energies at each step differ between petrochemical and bio-based polyethylene, like this second step in the degradation of LDPE SBC 818 and LDPE SEB 853 at which the chain scission reactions are the dominant one. The next step has an activation energy of approximately 110 kJ/mol, which can be associated with the  $\beta$  scission of C-C bond according to scheme 2 [21].



Scheme 2. The  $\beta$  scission of C-C bond

The last step is defined in literature as a stage where the chain termination is observed at DTG max. 460–480°C, the small peak above 500°C contributes to the evaporation of low volatile compound. In the case of bio-based polyethylene LDPE SBC 818 and LDPE SEB 853 high react order is observed, suggesting that all these reactions as termination and low volatile compound evaporation occur at the same time above 500°C. Completely different behavior is observed for LDPE SPB 681 samples. They exhibit a six-step thermal degradation in the air. The activation energy at the first step is the same as for the rest of the bio-polyethylene grades. It can be stated that the degrada-

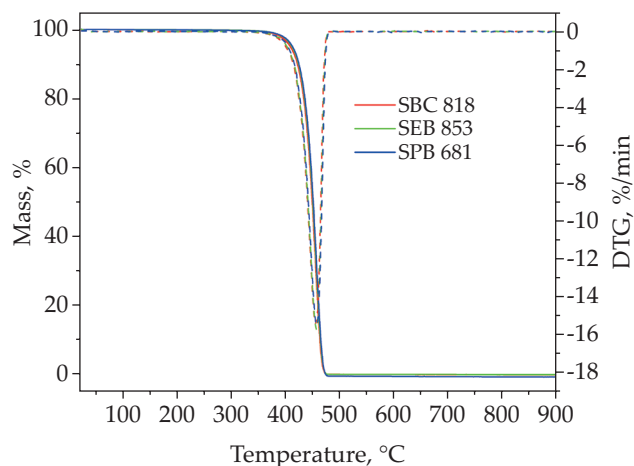


Fig. 3. TG and DTG curves of bioLDPE in nitrogen atmosphere

tion mechanism at this step is equivalent for all polyethylene grades. The second step, between 350–370°C, also has a similar activation energy and is related to  $\beta$  C-H bond scission. The four next steps have a lower activation energy between 80 and 110 kJ/mol, and according to Peterson *et al.* [22], is responsible for all oxygen-initiated depolymerization reactions [23]. The activation energies in this range correspond to the formation of ketones and alcohols [20]. The reaction orders are low, all below one, suggesting that one specific reaction is carried out simultaneously. The reactions at these four steps are related to the stripping of H atoms by free radicals. The peroxy radicals react with alcohols or polymer chains in this reaction, which tend to cleavage with increasing temperature [25]. The last step in this example is responsible for the evaporation of low-volatile compounds. The deconvolution of DTG peaks of bio polyethylene LDPE SBC 818 and LDPE SEB 853 can be reasonable to better investigate thermal degradation in the air. The high reaction order can suggest that some reactions can overlap each other. Figure 2 presents the possible deconvolution DTG peaks to six-step degradation for LDPE SEB 853 at a heating rate of 5°C/min.

The thermogravimetric measurement in an inert atmosphere of bio-based polyethylene has a similar curve for all three grades. Only one step degradation is observed (Fig. 3), and the DTG peak is located at the same temperature (457°C). Also, each sample's temperature at the 5% mass loss is the same.

The degradation of bio-based polyethylene in a nitrogen atmosphere was also analyzed according to the activation energies. The Kissinger method helped to develop the activation energy at the maximum DTG. The difference in activation energy values is 20 kJ/mol

Table 3. TGA data and activation energy for bioLDPE in nitrogen atmosphere

bioLDPE grade	$T_{5\%}$ , °C	$T_{\max}$ , °C	DTG, %/min	Kissinger $E_a$ , kJ/mol
SBC 818	409.7	457.3	-15.50	286.64
SEB 853	412.5	457.3	-15.77	266.01
SPB 681	413.9	457.7	-15.55	246.37

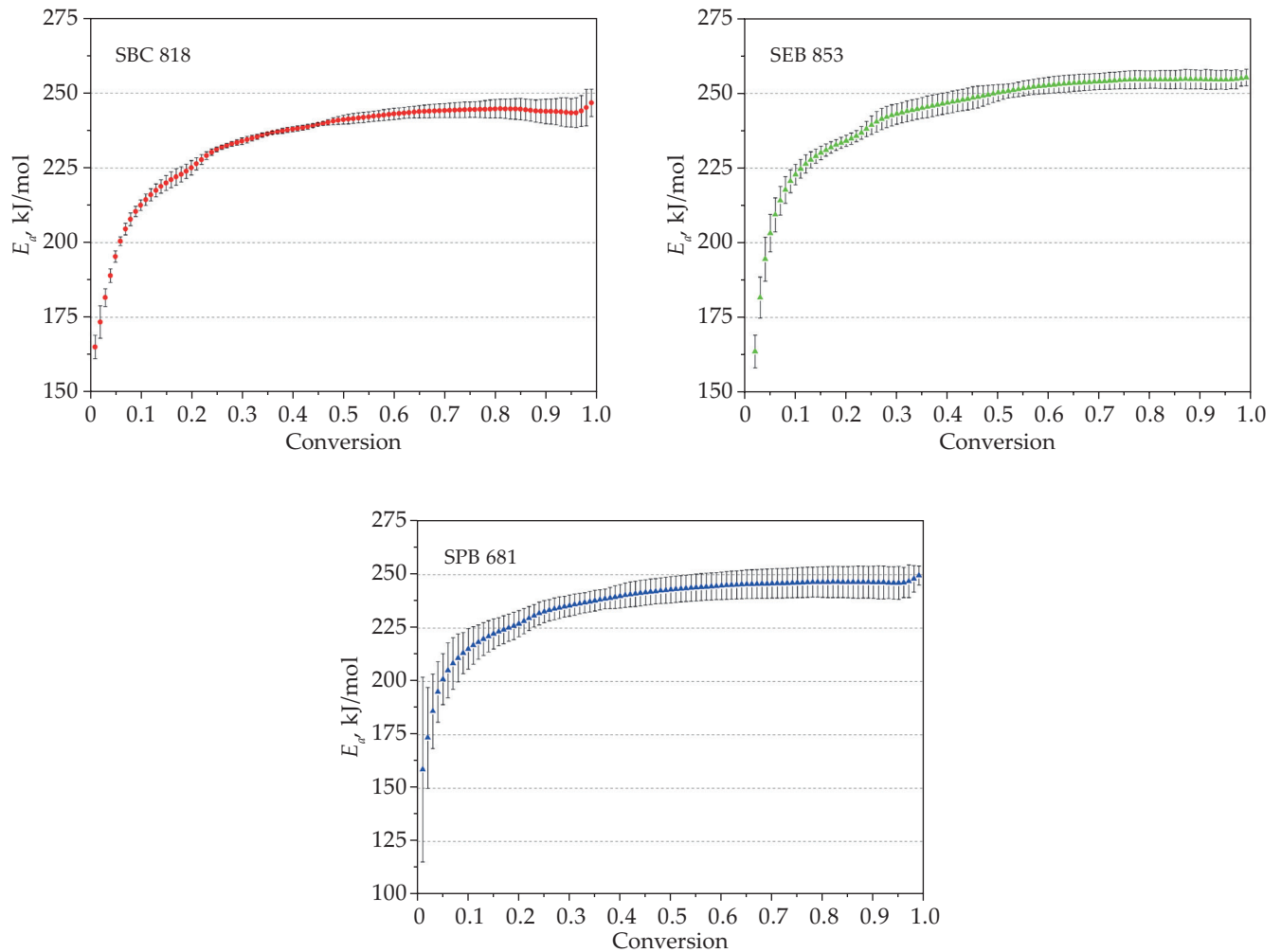


Fig. 4. The dependence of activation energies on conversion calculated according to the Ozawa-Flynn-Wall isoconversional kinetics method for thermal degradation of bioLDPE in nitrogen atmosphere

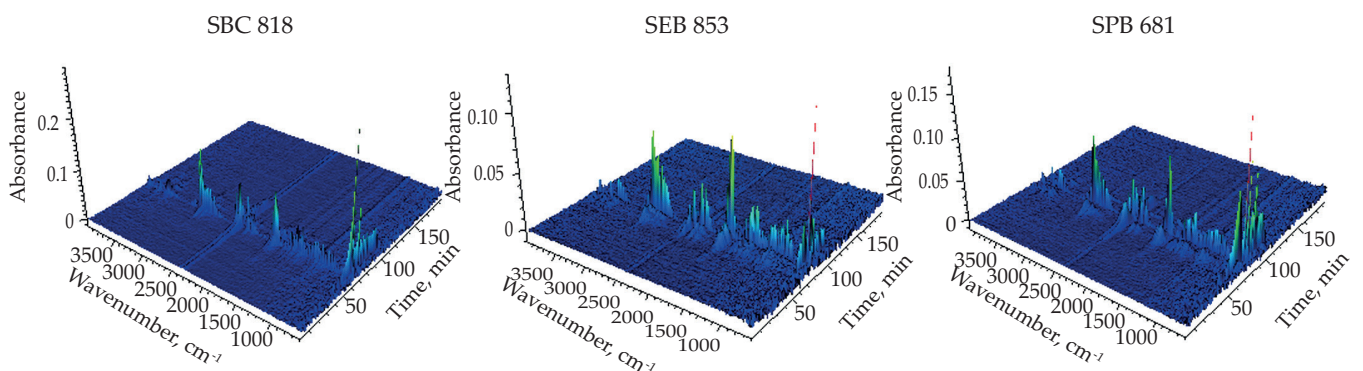
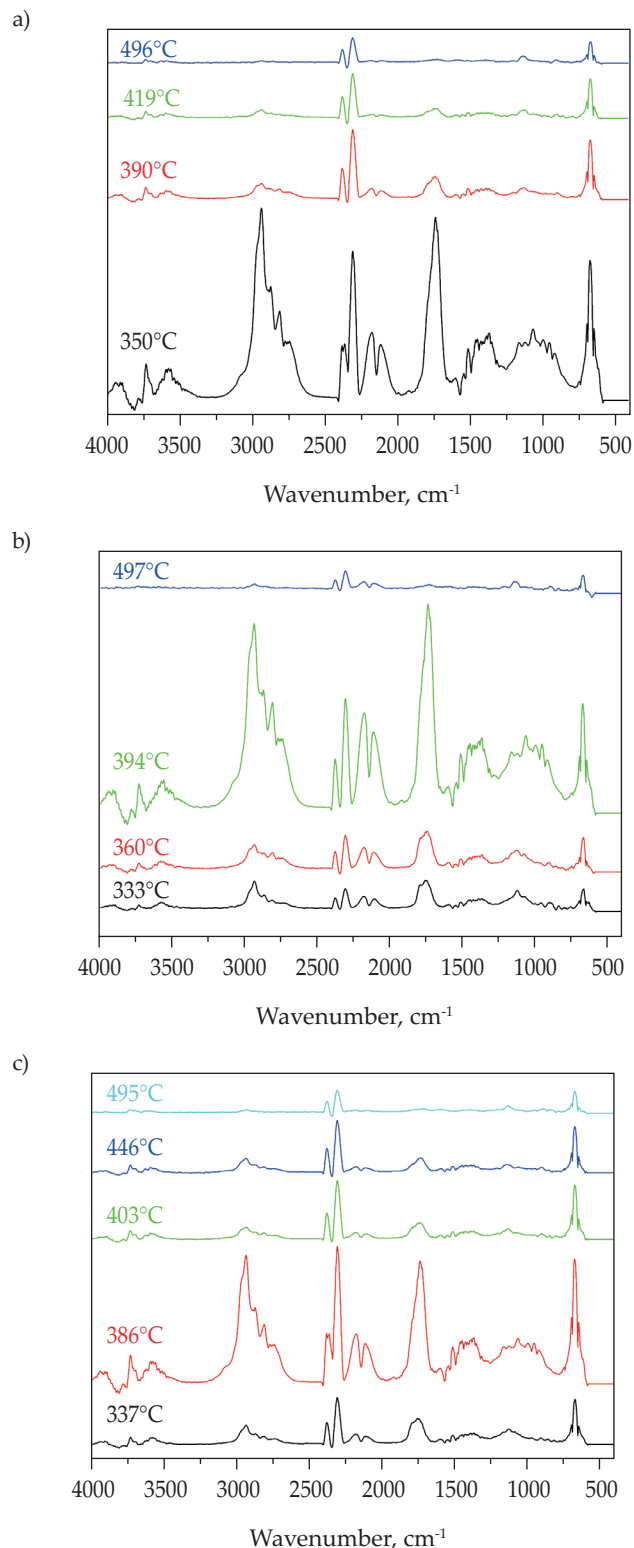


Fig. 5. FTIR spectra of gaseous products as a function of time during TGA analysis

between grade LDPE SBC 818 – LDPE SEB 853 and LDPE SEB 853 – LDPE SPB 681. These high activation energies are more likely to appear for the thermal degradation of high-density polyethylene [15, 26]. The average value of activation energy for thermal degradation of LDPE is 215 kJ/mol according to Aboulkas *et al.* [15, 27] and 130.04 to 193.10 kJ/mol according to Wang *et al.* [28]; both ener-

gies were obtained by the Kissinger method [15]. Also, the activation energies calculated using the Ozawa method showed a tendency where the activation energy is higher for HDPE than LDPE. According to Park *et al.* [28], the activation energy for HDPE degradation is 210–258 kJ/mol and 125–203 kJ/mol for LDPE. The measured kinetics for bio-based low-density polyethylene grades align with the

values previously calculated for high-density polyethylene. The activation energies calculated using the Ozawa-Flynn-Wall method (OFW) increase to reach a steady state with the increase in conversion. The steady state for LDPE SBC 818 is slightly below 250 kJ/mol, LDPE SEB 853 is above, and LDPE SPB 681 is approximately 250 kJ/mol.



**Fig. 6.** FTIR spectra of gaseous products taken at selected temperature during TG-FTIR analysis: a) SBC 818, b) SEB 853, c) SPB 681

The average dissociation energy for C-C bond is 348 kJ, so half of this value is 174 kJ, which means that this degradation is not only chain scission but also the chain branching, which limitations in higher temperature leads to degradation initiated by random chain scission [21, 22]. The degradation in an inert atmosphere is a steady process compared to the degradation in air.

During the TGA in the air atmosphere, there are a lot of evolving gases. The additional analysis of these gases performed by FTIR allows the identification of gaseous degradation products. Figure 5 presents 3D graphs of evolved gases' FTIR spectra as a time function. Over the time of thermal degradation of the sample, different peaks appear in the FTIR spectrum and their absorbance changes. The Gram-Schmidt graphs distinguished four peaks for LDPE SBC 818, LDPE SEB 853, and six peaks for LDPE SPB 681. This is strictly correlated with the above analysis of steps in the degradation of those polymers. In Figure 6 are presented FTIR spectra corresponding to those peaks. The highest absorbances are related to the highest mass loss rate, where a high number of gases evolve during oxidative atmosphere degradation. Data collected from the TGA measurement aligns with the Gram-Schmidt graphs, but the temperatures and mass loss are slightly different than those collected from the previous thermogravimetric analysis for kinetic properties. Differences between temperatures per each degradation step are approximately 1.3°C for LDPE SBC 818, 26.8°C for LDPE SEB 853, and 3°C for LDPE SPB 681. Those differences can be caused by higher airflow during the test. Nevertheless, the changes can be accepted. The more concerning is the shift of the peak with the highest mass loss rate; for LDPE SBC 818, the highest amount of evolved gases is observed at the first step, but data from Table 1 states that the highest mass loss is at the second step, for LDPE SEB 853 this step is shifted to the higher temperatures and for LDPE SPB 681 for lower.

Moving on to the analysis of gaseous products of combustion bio-based polyethylene in air atmosphere, Table 4 contains all distinguished peaks from FTIR spec-

**Table 4.** Peaks identified in FTIR spectra of gases from TGA analysis [29, 30]

Wavenumber, cm <sup>-1</sup>	Assignment
3731	O-H (H <sub>2</sub> O)
3575	
2935	-CH <sub>2</sub>
2362	-CO <sub>2</sub>
2306	-CO <sub>2</sub>
2175	-CO
2115	-CO
1737	C=O
1365	O-H (alcohol)
1064	C-O (primary alcohol)
673	CO <sub>2</sub>



tra. A peak appearing in all samples is characteristic for bond O-H in water. The same regards peak distinct for C-H band and  $-\text{CO}_2$ . Their absorbance is the highest in spectra at which the mass loss rate was the highest. They also appear during other degradation steps with lower absorbance but on the same level. The difference between absorbance or appearance of peaks is noted for C=O and C-O; they are related to the oxidized structure. The TGA-FTIR measurement for petrochemical high-density polyethylene did not show evolving carbonyl compounds during pyrolysis [29]. The same thing was noticed by Tidjani *et al.* [30], who analyzed gaseous products of combustion of LLDPE. They also tested exposed to  $\gamma$ -radiation LLDPE. During pyrolysis, samples treated with radiation in the air atmosphere exhibit carbonyl compounds in gaseous form. The  $\gamma$ -rays were used in this study as a promoter of degradation. The bioLDPE samples show the same characteristic where the peak of the carbonyl group appears at  $1737\text{ cm}^{-1}$ , and its absorbance differs at all degradation steps. The absorbance increases to gain maximum at the step with the highest mass loss and then decreases to finally not appear at the last step for all samples. Another peak also suggests evolving oxidized products at  $1064\text{ cm}^{-1}$  characteristic for C-O bond in primary alcohol, and, like the one for carbonyl compounds, did not appear at the last step of degradation.

## CONCLUSIONS

The comprehensive analysis of the degradation kinetics, coupled with thermogravimetric analysis, provides insights into the thermal decomposition of bio-based polyethylene in both air and nitrogen environments. Typically, the degradation process of polyethylene in air consists of four distinct steps. However, this study has unveiled that LDPE SPB 681 follows a six-step degradation process. It can be affirmed that the DTG temperatures in the presence of air for each degradation step are higher for bio-polyethylene's compared to their petrochemical counterparts. The earlier assumption regarding the upward shift of degradation stages to higher temperatures for these two bio-polyethylene grades may be erroneous, as suggested by the analysis of activation energies. Instead, it can now be asserted that the initial two degradation steps have amalgamated into a single significant stage. The activation energies associated with each step correlate with the underlying reactions during polyethylene decomposition, such as chain scission, the formation of functional groups, and polymer chain termination. In an inert atmosphere, the thermal degradation of all the samples occurs in a one-step process, with activation energies aligning closely with existing literature data, particularly when considering petrochemical HDPE. Examination of the gases emitted during thermal degradation in air has previously been associated in the literature with the degradation of LLDPE exposed to  $\gamma$ -radiation. The distinctive peaks observed in the FTIR

spectra of the evolved gases correspond to C=O and C-O bonds, with variations in absorbance observed across different degradation stages. Typical thermal decomposition products include  $\text{H}_2\text{O}$ ,  $-\text{CH}_2$ ,  $-\text{CO}_2$ , and  $-\text{CO}$ . The analysis enables understanding the processes occurring during the thermal degradation of bio-based polyethylene and comparing them with the well-documented thermal decomposition of petrochemical polyethylene.

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