INFLUENCE OF SAMPLE PREPARATION ON THERMAL DECOMPOSITION OF WASTED POLYOLEFINS–OIL MIXTURES

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Significant influence of sample preparation on thermal decomposition of polyolefin–technological oil mixtures was proved during tests. Samples of polymer–oil mixtures were prepared with two methods: reducing size and components mixing and soaking in temperature 170°C. Soaking causes decreasing thermal stability of the charge. This fact manifests itself in decreasing of thermal decomposition temperature in laboratory scale, as well as in change of characteristic decomposition temperatures during thermogravimetric analyses. Data analysis was performed with the use of classic method based on Arrhenius kinetic equation and three-parameter model. The influence of sample composition and preparation method on values of three-parameter equation coefficients was observed.

Introduction

One of more promising solutions in waste management of chosen waste plastics is thermal processing, where as a result liquid products are obtained, which are used in production of liquid fuels [1–3]. Decomposition of polymers, especially polyolefins, with addition of catalysts is the prevailing subject in literature [4–9]. Solutions connecting thermo-catalytic stages with hydrogenation of decomposition products are also known [6]. On the other hand, one proposes decomposition of polymers-solvents systems known as technological oils [10–15]. The solution allows mitigating conditions of the process and increasing its yield, but it is also connected with risk of introduction undesirable components (e.g. sulfur compounds and too much aromatic hydrocarbons) into products together with technological oil. Majority of works connected with the subject concentrate on thermal decomposition stage, paying minor attention to substrates preparation. Latest investigations revealed that, additional charge preparation stage before thermal decomposition significantly influences the process [16]. The proposed process, called soaking, consists in polymer digestion in technological oil in elevated temperature (150–180°C) [17, 18]. The technology of such preparation of polyolefin–paraffin oil mixture in scale of three reactors (4 m³ each), which are put together with six currently used thermal decomposition reactors (30 m³ each), has been implemented in Polish factory in Zabrze and Grupa LOTOS S. A. in Jasło[19].

Aim of the work

In the present work two variants of substrates preparation in polymer–technological oil system were compared. The first one consists in polymer grain size reduction and mechanical mixing together with oils. In the second case, thermal preparation called 'soaking' was used, during which polymers digestion in oils is observed. The influence of sample preparation on its thermal decomposition in laboratory scale was investigated and changes in its thermal properties were found using TG/DTG measures.

Experimental

Materials

Substrates used in analyses were: polyethylene LDPE, polypropylene PP and technological oils (TO): paraffin oil (TO1 – M_{av}=295 g mol⁻¹; iodine number 5 g I_2/100 g; S=0.35%, t_b=61–360°C), vacuum distillate after hydrocracking (TO2 – M_{av}=401 g mol⁻¹; d=0.878 g cm⁻³; iodine number 2.1 g I_2/100 g; S=100 ppm, t_b=69–362°C). With regard to availability of paraffin oil in Poland and thereby to its applicability in industrial processes, in further investigations more attention was paid to its mixtures with polymer samples.

Methods

Thermogravimetric measures were carried out in MOM OD-103 derivatograph in following condi-

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tions: platinum crucible, sample mass 15 mg, final temperature 800°C, heating rate q=10 K min^{-1}, inert atmosphere (N$_2$) (gas flow rate 12 cm^3 min^{-1}).

Analyses of thermal decomposition in laboratory scale (sample mass 50 g) were carried out within temperature range from ambient to 450°C with average heating rate 3 K min^{-1}. Samples were placed in glass reactor with capacity of 250 cm^3, which was located in thermostat. It provided for maintaining comparable conditions of process, which is accompanied by strong energetic effects. Condensation of liquid products took place in water cooler.

Thermal analysis of polyolefin–oil mixtures

Thermal analysis was applied for samples containing LDPE (because of their highest content in wastes) and PP together with paraffin oil. Thermal properties of samples containing 25% of paraffin oil were compared. The samples were prepared with using two methods: the first one consisted in reducing size of a sample and mixing components, the second one was soaking, as described above, carried out in temperature 170°C. Amount of technological oils equaled 25%.

Both thermogravimetric measures (samples No. 1–10, sample mass ca. 15 mg) and laboratory tests (samples No. 1'–10', sample mass 50 g) were carried out for following samples (in brackets: sample number):

PP	(1–1')
PP+TO1	(2–2')
PP+TO1 (soaked)	(3–3')
PP+TO2	(4–4')
PP+TO2 (soaked)	(5–5')
LDPE	(6–6')
LDPE+TO1	(7–7')
LDPE+TO1 (soaked)	(8–8')
LDPE+TO2	(9–9')
LDPE+TO2 (soaked)	(10–10')

Results and discussion

Thermal analysis

TG and DTG curves for analyzed samples are presented on Fig. 1. We can set apart two decomposition stages in case of samples containing technological oil (samples No. 2, 3, 5 and 6): the first one correspond-
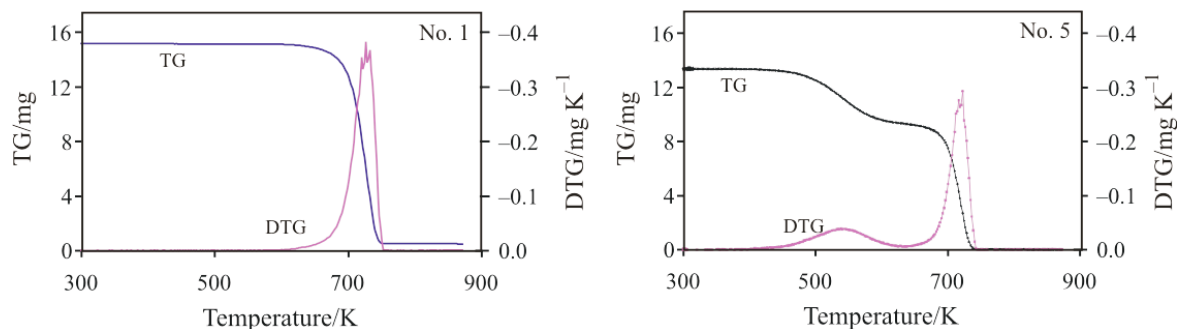

Fig. 1 Comparison of selected samples TG/DTG curves (samples No. 1 and 5 acc. to Table 1)

Table 1 Values of characteristic decomposition temperatures, t_i and t_m, in microscale

No.	Sample	Temperature/°C			
		I peak		II peak	
		t_i	t_m	t_i	t_m
1	PP*	–	–	420	460
2	PP+TO1	85	279	420	460
3	PP+TO1 (soaked)	93	289	418	454
4	PP+TO2	87	283	422	460
5	PP+TO2 (soaked)	99	291	402	452
6	LDPE*	–	–	428	469
7	LDPE+TO1	83	279	427	469
8	LDPE+TO1 (soaked)	91	291	413	450
9	LDPE+TO2	87	285	427	467
10	LDPE+TO2 (soaked)	100	295	412	448

* in all tables samples without technological oil

ing to distillation and oil decomposition, the second one is connected with polymer decomposition. It confirms effects observed in previous investigations [10, 11]. There were characteristic temperatures determined basing on DTG curves, t_i and t_m, which are temperature of both beginning and maximum of DTG peak, respectively Table 1.

Analysis of characteristic temperatures t_i and t_m points that introducing only technological oil into sample during microscale analyses does not significantly influence on position of thermal decomposition peak of polymer (comparison of samples No. 1 and 2, as well as No. 4 and 5). There is polymer thermal stability decreasing observed (even 19 K lower for sample No. 6) only after soaking. At the same time, there is increasing of paraffin oil decomposition characteristic temperatures observed from 8 to 10 K.

As opposed to thermogravimetric analyses, where mass loss is measured of conversion degree (α), there was necessity of its different defining in laboratory tests, i.e. as a ratio of liquid products amount to total products amount. Basing on obtained results, there were characteristic decomposition temperatures determined: initial (t_i), 50% conversion ($t_{0,5}$) and 90% conversion temperature ($t_{0,9}$), Table 2.

Table 2 Temperatures t_i, $t_{0.5}$, $t_{0.9}$ for thermal decomposition of analyzed samples

No.	Sample	Temperature/°C		
		t_i	$t_{0.5}$	$t_{0.9}$
1'	PP*	400	424	433
2'	PP+TO1	390	419	433
3'	PP+TO1 (soaked)	386	412	431
4'	PP+TO2	387	417	433
5'	PP+TO2 (soaked)	381	410	430
6'	LDPE*	417	442	448
7'	LDPE+TO1	413	440	447
8'	LDPE+TO1 (soaked)	407	432	444
9'	LDPE+TO2	414	439	446
10'	LDPE+TO2 (soaked)	406	432	441

*in all tables samples without technological oil

Analysis of obtained results shows beneficial influence of technological oil addition on the process. Simultaneously, there are no two separate decomposition stages observed for samples containing said oil, as it was in TG/DTG analyses described above. The most interesting observation is however significant change of decomposition characteristic temperatures, depending on sample preparation method. There is decomposition temperature decreasing observed in laboratory scale tests for samples No. 2', 4', 7' and 9' (polymer+technological oil prepared mechanically)

comparing with samples without additives (samples No. 1' and 6'). Decomposition temperature decreasing is more clearly visible for soaked samples as well in laboratory scale (samples No. 3', 5', 8' and 10') as in microscale (samples No. 3, 5, 8 and 10).

In case of thermogravimetric analyses of polymer–technological oil mixtures it was observed (regardless of preparation method) that thermal decomposition proceeds in two stages. The first one is connected with distilling oil off and its partial decomposition, the second one is related to polymer decomposition. The effect is not observe for samples with higher mass. Hence, there are difficulties with comparing both processes for the sake of different scales.

Kinetic methods

Methods based on Arrhenius kinetic equation leading to determination of kinetic parameters, so called single kinetic triplet $f(\alpha)$–E–A [20–24], are often used in analysis of thermogravimetric data. Within this area, many methods using measurements under dynamic conditions for one, as well as for different heating rates, have been worked out. There are review works often appearing in literature, which discuss different possibilities within this field, e.g. in 1998–2005 [25–28]. Analysis of thermogravimetric data obtained for one heating rate was carried out with the use of both classic method and three-parameter equation.

Classic method

Kinetic equation for dynamic conditions has form:

$$\frac{d\alpha}{dT}=\frac{A}{q}f(\alpha)e^{-E/RT}, \ q=\frac{dT}{d\tau}=const>0 \qquad (1)$$

which after separation of variables becomes:

$$g(\alpha)=\int_0^\alpha \frac{d\alpha}{f(\alpha)}=\frac{A}{q}\int_{T_i}^T e^{-E/RT}dT, \ T_i=0 \ K \qquad (2)$$

The left side of Eq. (2), $g(\alpha)$, is called mass integral, while right one – temperature integral.

One of the possibilities of Eq. (2) expressing is [29]:

$$g(\alpha)=\frac{AE}{qR}p(x)$$

where

$$p(x)=\frac{e^{-x}}{x^2}\left[\frac{1-2/x}{1-m(1/x)^2}\right], \ x=E/RT \qquad (3)$$

There are following cases for different m values [29]:

1. $m=0$ for the Coats–Redfern equation

2. $m=4$ for the Gorbachev equation
3. $m=5$ for the Agrawal equation
4. $m=6$ for the Li equation.

There are other solutions in this field, for example Senum and Yang approximation [30], in which it is introduced mistake sometimes [31]. Complex study one can find in valuable books [32, 33] or very interesting review [31]. In this paper Coats–Redfern approximation was used due to it is one of the most often using in literature.

Basing on considerations of Coats and Redfern [34, 35] the following solution of Eq. (2) was obtained in simpler form [36]:

$$g(\alpha)=\frac{ART^2}{qE}e^{-E/RT} \qquad (4)$$

$$\ln\frac{g(\alpha)}{T^2}=\ln\frac{AR}{qE}-\frac{E}{RT} \qquad (5)$$

Referring to estimation problem of kinetic parameters from Eq. (1), i.e. single kinetic triplet [20–24], the following $f(\alpha)$ selection criteria were proposed by authors:

- analysis of N=12 models: F1, F2, F3, R1, R2, R3, A2, A3, D1, D2, D3 and D4 according to [37] was carried out by substitution of particular forms of $g(\alpha)$ function into Eq. (5); as a result, the next sets of kinetic parameters E–A was obtained. Relations $\ln A$ *vs.* E is so called kinetic compensation effect (KCE) [31, 36, 38–42] or sometimes isokinetic effect (IE) [43, 45]. It very often reveals model concentration in three groups: high values of E – model D, low values of E – model A, medium values of E – models F, R and their linear combinations [40, 41].
- significance of $g(\alpha)$ was taken according to the value of linear regression determination coefficient $r^2>0.99$ for Eq. (5),
- values of averaged activation energy were calculated (for models fulfilling condition 2) from relationship [43]:

$$\overline{E}=\frac{1}{N}\sum\frac{E}{b} \qquad (6)$$

There are the papers in which only the most probably models are taken into account [44],

- values of averaged pre-exponential factor were calculated from relationship, which has been derived for models fulfilling condition $g(\alpha_m)=1$ in Eq. (4) [43, 45] and, which also is the Kisssinger law:

$$\ln\overline{A}=x_m+\ln(x_m q/T_m), \; x_m=E/RT_m \qquad (7)$$

In case when $T_m=T_{iso}$ and $k_m=x_m q/T_m=k_{iso}=$const. – the relationship is also called isokinetic effect

[43, 45]. Relation (7) is even covered by American Society for Testing and Materials [46].

The results are presented in Table 3. The distance of E towards average values for samples containing PP equals 11.1% and for samples containing LDPE 22.0% (Table 3).

Addition of oil (samples 2, 4, 7 and 9 in Table 3) causes increase of activation energy in comparison with samples 1 and 6, while soaking (samples 3, 5, 8 and 10) leads to its decreasing in relation to samples 2, 4, 7 and 9, but the value is higher than this for polymer samples (samples 1 and 6).

Analysis of obtained results indicates existing of isokinetic effect, that is rectilinear relationship between logarithm of pre-exponential factor and activation energy [43, 45]. When all obtained values of E and $\ln A$ (there were 120 points on the plot obtained for 10 samples) were taken into consideration the resulted straight-line had linear regression determination coefficient $r^2=0.9796$. When only averaged values, presented in Table 3, were analyzed the resulted straight-line (6) had the following analytical form:

$$\ln\overline{A}=1.56\cdot10^{-4}\cdot\overline{E}-3.435, \; (r^2=0.9910) \qquad (8)$$

The existence of isokinetic effect in case of analyzed samples – Fig. 2 (the case A acc. [37]) – results from the fact of their chemical similarity, not from selection of $f(\alpha)$ or $g(\alpha)$ function. At the same time it was observed that logarithm of reaction rate in temperature T_m shows little variability within range –5.30
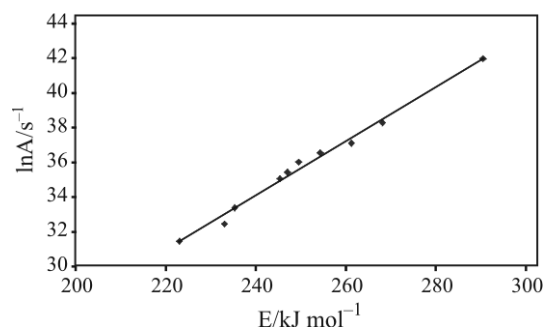

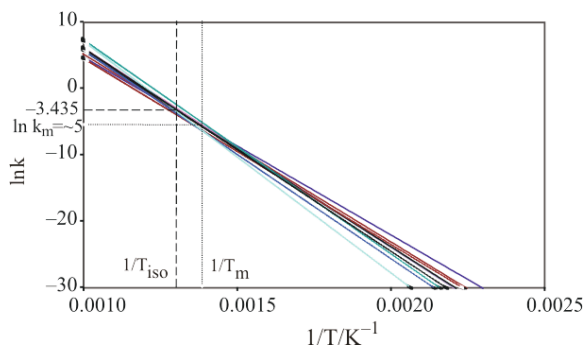**Fig. 2** Isokinetic effect for analyzed samples

Fig. 3 $\ln k$ *vs.* $1/T$ curves for analyzed samples after correlation (Arrhenius plot) – cescription in the text

Table 3 Averaged values of activation energy, pre-exponential factor and natural logarithm of rate constant in point T_m of thermal decomposition of analyzed samples

No.	Sample	$\bar{E}$/kJ mol^{-1}	$\ln\bar{A}$	$\bar{A}$/s^{-1}	Models fulfilling cond. $r^2 > 0.99$	Max. r^2	$T_m^{\,a}$/K	$\ln k_{iso} = x_m g/T_m$	$\ln k_m = \ln A - x_m$ [b]
1	PP*	222.9	31.489	4.74×10^{13}	D3, R3	0.9902	733	–5.300	–5.091
2	PP+TO1	249.5	36.045	4.51×10^{15}	D3, R3	0.9907	733	–5.188	–4.895
3	PP+TO1 (soaked)	235.2	33.398	3.20×10^{14}	D3, D4, R2, R3	0.9912	727	–5.230	–5.521
4	PP+TO2	247.0	35.435	2.45×10^{15}	D3, R2, R3	0.9910	733	–5.198	–5.092
5	PP+TO2 (soaked)	245.2	35.090	1.73×10^{15}	D2, D3, D4, R2	0.9929	725	–5.183	–5.597
6	LDPE*	233.0	32.481	1.28×10^{14}	D2, D3, D4, R2, R3	0.9926	742	–5.281	–5.283
7	LDPE+TO1	268.0	38.306	4.33×10^{16}	F1, D3, R2, R3	0.9928	742	–5.140	–5.143
8	LDPE+TO1 (soaked)	261.1	37.109	1.31×10^{16}	D2, D3, D4, R2, R3	0.9933	723	–5.115	–5.332
9	LDPE+TO2	290.4	42.011	1.76×10^{18}	D2, R2, R3	0.9916	740	–5.055	–5.190
10	LDPE+TO2 (soaked)	254.2	36.569	7.66×10^{15}	F1, D2, D3, R2	0.9927	721	–5.136	–5.841

[a]determined experimentally, [b]according to Arrhenius law; * – in all tables samples without technological oil

to –5.05 for all samples. On the other side, the value of T_{iso}=768 K, which corresponds to pencil of lines intersection point in coordination system of $\ln k$ vs. $1/T$, Fig. 3, results from slope of Eq. (8), which is equal to $1/RT_{iso}$. In case of all samples $T_{iso}>T_m$, while $\ln k_{iso}$=–3.435.

If one forces the slope $\equiv 1$ upon the linear relation $\ln A$ vs. x_m then k_m passes into k_{iso} and the resulted straight-line had the following analytical form:

$$\ln \overline{A} = \frac{\overline{E}}{RT_m} - 5.398 \text{ or } \ln A = x_m - 5.398 \ (\rho^2 = 0.9798) \quad (9)$$

The solution of estimation problem of kinetic parameters $f(\alpha)$–E–A for samples of polyolefines with technological oil addition was proposed in present work. However, the data obtained this way do not confirm effects visible in laboratory scale (Table 2), where introduction of technological oil causes decreasing of characteristic decomposition temperatures, and soaking in addition intensifies the effects. In addition, existence of isokinetic effect makes unambiguous interpretation of obtained data difficult. Therefore, it seems that carried out analysis is not much useful for description of thermal decomposition of complicated systems: polyolefins-technological oils.

In case of the first decomposition stage connected with technological oil decomposition, the problems connected with estimation of kinetic triplet $f(\alpha)$–E–A came across. They resulted mainly from the fact that condition 2 was fulfilled only for sample 3 (F1, r^2=0.9914). After lowering this criterion to $r^2>0.98$, the calculated activation energies varied within range of 50–62 kJ mol^{-1}.

Three-parameter equation

Analogically as in previous work [10] three-parameter model, which connects conversion degree (α) directly with temperature (T) without mass integral generation $g(\alpha)$, was used for description of thermal decomposition. The model is represented by equation [47]:

$$\ln \alpha = a_0 - \frac{a_1}{T} - a_2 \ln T, \ 0 < \alpha \leq 1 \quad (10)$$

where a_2 is recognized as characteristic coefficient related to rate of thermal decomposition.

It was observed in other works [11, 48–51] that a_2 increasing is concurrent with linear increasing of both a_0 and a_1. In connection with this and work [48] a_2 is recognized as priority quantity. There were two relationships set apart from investigation for samples containing PP and LDPE:

PP: $a_0 = 68.21 + 6.19 a_2 \ (r^2 = 0.9998)$

      $a_1 = 20697 + 410 a_2 \ (r^2 = 0.9998)$

LPDE: $a_0 = 73.05 + 7.01 a_2 \ (r^2 = 0.9997)$

      $a_1 = 32209 + 432 a_2 \ (r^2 = 0.9996)$

One also may present common relationships for all analyzed samples (PP and LDPE) at the cost of little worsening of correlation:

$a_0 = 71.53 + 6.57 a_2 \ (r^2 = 0.9912)$

$a_1 = 22391 + 427 a_2 \ (r^2 = 0.9987)$

Significance level in all cases was 0.0000.

After differentiation and transformation of Eq. (10) we obtain relative rate r, expressed by formula [41]:
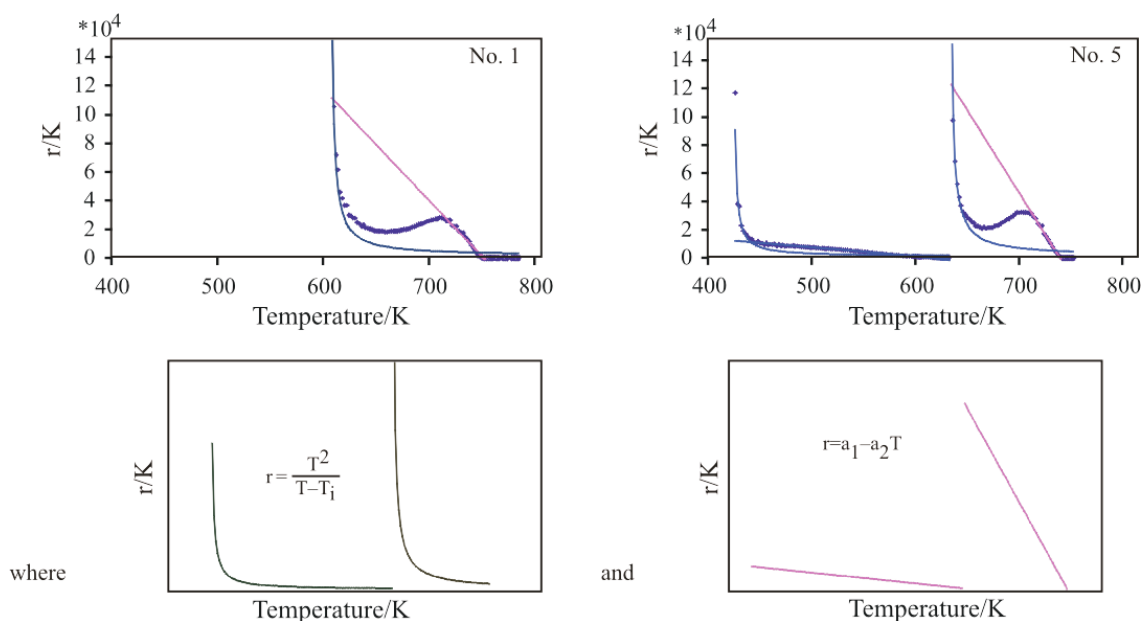

Fig. 4 Relationship r vs. T for selected samples (samples No. 1 and 5 acc. to Table 1)

Table 4 Values of coefficient a_2 and determination coefficient R^2

No.	Sample	Temperature/°C			
		I peak		II peak	
		a_2	R^2	a_2	R^2
1	PP*	–	–	219	0.9855
2	PP+TO1	51	0.9970	275	0.9712
3	PP+TO1 (soaked)	65	0.9916	314	0.9910
4	PP+TO2	53	0.9991	284	0.9875
5	PP+TO2 (soaked)	69	0.9897	327	0.9906
6	LDPE*	–	–	254	0.9914
7	LDPE+TO1	58	0.9992	278	0.9881
8	LDPE+TO1 (soaked)	70	0.9974	490	0.9860
9	LDPE+TO2	61	0.9908	292	0.9928
10	LDPE+TO2 (soaked)	75	0.9969	501	0.9983

*in all tables samples without technological oil

$$r=\frac{d\alpha/dT}{\alpha}T^2=-\frac{d\ln\alpha}{d(1/T)}=-\frac{DTG}{m_i-TG}T^2=a_1-a_2T \quad (11)$$

Further analysis of Eq. (11) leads to temperature relationship (12) determined as activationless temperature profile of 0th order [49, 52]:

$$r=\frac{T^2}{T-T_i}=T+T_i+\frac{T_i^2}{T-T_i} \quad (12)$$

There were straight-line ranges set apart on r vs. T plots (Fig. 4), which were plotted basing on both relationship (11) and coefficients a_1 and a_2 from Eq. (10). The ranges correspond to wide set of α values: 0.1–0.99 for the first stage and 0.27–0.98 for the second one. This fact confirms previous conclusions that using relative rate of thermal decomposition is much more convenient than hitherto used DTG data (Fig. 1). Values of both a_2 and determination coefficient r^2 for every stage is presented in Table 4. Three-parameter equation follows from the van't Hoffs isobar, which determines the dissociation enthalpy that is quantity proportional to the ratio of $\ln\alpha_{eq}/(T_{eq}^{-1}-T^{-1})$. The relation (10) becomes applicable using three a's approximate constans [33]. Due to a fact that one can express this relation in simple form (11) one can state that increase of a_2 value provides to increase of reaction rate in terms of $d\alpha/dT$, but not always in terms of $d\alpha/d\tau$, which is primary form [32, 53]. The higher is value of a_2 the higher thermodestruction dynamics is observed. Our studies indicated that a_0 and a_1 increased together with a_2.

Obtained values of Eq. (10) coefficients differ from these obtained in works [10, 11] for analogical systems, what is due to differences in thermal process conditions and thermobalance type.

Determined values of a_2 coefficient are relatively small, a_2=51–75, for the first stage of thermal decomposition, where physical processes (distillation and, to a less extent, technological oil thermal decomposition) dominate. At the same time, there is no influence of composition and preparation method on a_2 value observed. Thus, one may assume that it is approximately constant for analyzed samples and independent on above mentioned factors. Experimental points for the first stage are described by straight-line relationship (11) within wide range of conversion degree, α=0.03–0.99, and approximate to temperature relationship (12), i.e. 0-order activationless process [49, 52].

In case of the second stage connected with PP or LDPE decomposition (endothermic peak on DSC curves, e.g. [16]) coefficient a_2 takes on significantly higher values, a_2=219–501. The course of experimental points may be divided in three areas, while fundamental and leading relationship is Eq. (11). Within range $0<\alpha<0.05$ it may be approximated by temperature relationship (12), which appears for vast majority of thermal decomposition cases. There is straight-line relationship (11) observed within range $0.27<\alpha<0.98$. Within range $0.05<\alpha<0.27$ one may notice different kind of r vs. T relationship, which results from fact that TG curve does not reflect real transformations occurring in sample, but merely concurrent mass losses. Decomposition of polyolefins, which were subject of presented investigations, proceeds according to random-chain scission mechanism [7] and long polyolefin chains breaking (at the beginning average molecular mass is very large) leads to small amount of volatile products forming (insignificant sample mass changes, which are represented by DTG peak extension). As the decomposition process develops together with reducing of chains length, larger and

larger amount of volatile products is forming, what is registered as mass loss by thermobalance. There are two types of relationships within this range. There is linear relationship for samples No. 4, 6 and 7 analogical as described in works [49, 50, 52], which is characterized by reversed signs of coefficients of Eqs (10) and (11). It represents physical processes occurring in sample in case of model compounds (e.g. it was proved on example of coronene sublimation [52]). The relationship within mentioned range ($0.05 < \alpha < 0.27$) is polynomial in case of samples No. 1–3, 5, 8–10.

There is also significant influence of composition and sample preparation method observed on value of coefficient a_2 in the second decomposition stage – oil addition leads to its increasing of $\Delta a_2 = 24$–65, while after soaking of $\Delta a_2 = 95$–247.

Values of coefficient a_2 were higher for samples No. 1–5 than those observed for samples No. 6–10, of which decomposition proceeded in higher temperatures as well in microscale as in laboratory scale. Hence, one may set apart two groups of relationships for samples containing both polypropylene and polyethylene.

From above considerations on relationship r vs. T acc. to Eq. (11) follows that this kind of thermogravimetric data analysis allows drawing richer conclusions than those drawn from typical DTG data analyzing. Assessing only initial temperature of process, T_i, one may describe it by relationship (11) within wide range of conversion degree (in the first stage: $0.03 < \alpha < 0.99$; in the second one: $0.27 < \alpha < 0.98$), what represents transformations occurring in a sample.

In spite of significant differences in thermal decomposition, as well as in conversion degree (α) defining, there was dependence in different testing scales observed between coefficients of Eq. (10) (thermal analysis) and characteristic decomposition temperatures (Fig. 5) (laboratory scale). It is clearly visible that increasing of a_2 (which describes microscale data) is accompanied with characteristic decomposition temperatures decreasing in laboratory scale tests.
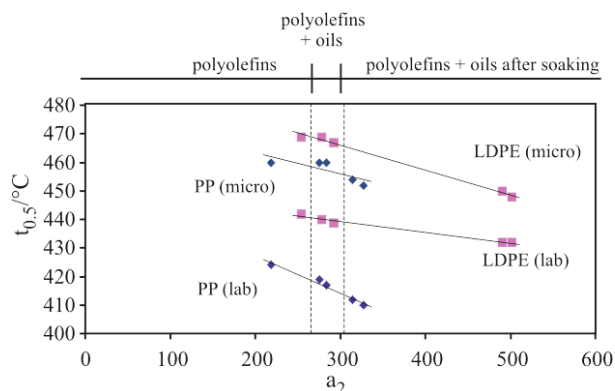

Fig. 5 Relationship between coefficient a_2 (microscale) and temperature corresponding to 50% conversion, $t_{0.5}$ (both micro- and laboratory scale)

One can also clearly set apart three temperature ranges corresponding with mixed and soaked samples without addition of oil.

Conclusions

The method for the preparation of polyolefin–oils mixtures was developed and a significant influence of sample preparation of such mixtures on thermal decomposition process was proved. The preparation includes so-called soaking at 170°C (150–180°C in industrial conditions) which enables further decomposition of the solution at higher temperature. Soaking causes a decrease of thermal stability of the charge. This decreases the temperature of thermal decomposition at the same time decreasing also the duration of the decomposition process.

A three-parameter model allows us to describe the process by linear relation (11) within the wide range of conversion degree (α). The influence of a type of oil and a method of preparation on the coefficients in Eq. (10) can be clearly observed. The introduction of oil increased the a_2 value, which corresponds to the decrease of the decomposition temperature in the laboratory scale. Soaking resulted also in the major increase in a_2 value and the significant decrease in the decomposition temperature in laboratory scale. The presented approach allows us to connect the analyses of thermal decomposition in micro- and laboratory scales.

The analysis of thermogravimetric data was performed by standard method using the Arrhenius kinetic equation. The method used based on the measurements under dynamic conditions for one heating rate in opposition to the so-called isoconversion methods for different heating rates that are used most often [20]. We also developed a novel method for the determination of activation energy and pre-exponential factor. This proved the presence of isokinetic effect originated from the chemical similarity of analyzed samples. It is worth mentioning that this factor has not been studied frequently. We confirmed that the standard method does not allow to show conclusively the effect of the addition of technological oil and the influence of soaking process on thermal decomposition of polyolefins.

Symbols

A	pre-exponential constant in Arrhenius equation, s^{-1}
$\overline{A}$	averaged pre-exponential factor, s^{-1}
a_0, a_1, a_2	coefficients of three-parameter Eq. (10)
Δa_2	increment of a_2
α	conversion degree, $0 \leq \alpha \leq 1$
α_{eq}	equilibrium conversion degree, $0 \leq \alpha_{eq} \leq 1$

b — coefficient models for: F and R $b=1$, A2 $b=1/2$, A3 $b=1/3$, D $b=2$

DTG — rate of sample mass change registered by thermobalance, mg K^{-1}

E — activation energy, J mol^{-1}

$\bar{E}$ — averaged activation energy, J mol^{-1}

$f(\alpha)$ — function of α depending on the reaction mechanism

$g(\alpha)$ — mass integral

m — indicator in Eq. (3)

m_i — initial mass of sample, mg

N — number of models

q — heating rate, K s^{-1}

$R=8.314$ J mol^{-1} K^{-1} — universal gas constant

r — relative rate of reaction, K

r^2, ρ^2, R^2 — determination coefficient for the linear and multiple regression, respectively, $0 \leq r^2, \rho^2, R^2 \leq 1$ (ρ^2 for slope$\equiv 1$)

$t, t_i, t_m, t_{0.5}, t_{0.9}$ temperature, characteristic temperatures of decomposition: initial (i), corresponding to maximal transformation rate (m), 50% conversion and 90% conversion, respectively, °C

T, T_m, T_{eq} — temperature, temperature corresponding to maximal transformation rate, equilibrium temperature (for which free enthalpy is 0), K

TG — mass values registered during thermogravimetric measure, mg

τ — time, s

$x=E/RT$

$x_m=\bar{E}/RT_m$ — dimensionless activation energy.

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