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Study of the thermooxidative degradation kinetics of poly(tetrafluoroethene) using iso-conversional calculation procedure

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Abstract The thermooxidative degradation kinetics of poly(tetrafluoroethene) (PTFE) in air flow has been studied at different heating rates (6, 10, 12 and 15 K min^{-1}) by non-isothermal differential thermal analysis (DTA). Six calculation procedures based on single TG curves and iso-conversional method, as well as 27 mechanism functions were used. The comparison of the results obtained with these calculation procedures showed that they strongly depend on the selection of proper mechanism function for the process. Therefore, it is very important to determine the most probable mechanism function. In this respect the iso-conversional calculation procedure turned out to be more appropriate. In the present work, the values of apparent activation energy E, pre-exponential factor A in Arrhenius equation, as well as the changes of entropy $\Delta S^{\neq}$, enthalpy $\Delta H^{\neq}$ and free Gibbs energy $\Delta G^{\neq}$ for the formation of the activated complex from the reagent are calculated. All calculations were performed using programs compiled by ourselves.

Keywords Kinetic parameters · Non-isothermal kinetics · Thermogravimetric analysis · Thermooxidative degradation · Poly(tetrafluoroethene)

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Introduction

Fluoropolymers are technical polymers with very special properties and applications. The most important fluoropolymer is poly(tetrafluoroethene) (PTFE or Teflon) consist of a fluorinated straight chain polymer, $(\text{–CF}_2\text{CF}_2\text{–})_n$. Discovered in 1938 by Plunkett, in 1994 the average annual global consumption of fluorinated polymers was 43,500 metric tones but in 2004 world consumption of fluoropolymers reached almost 133,000 metric tones, with a projected annual increase of 7%. PTFE being the dominant fluoropolymer, accounting for 59 mass% of global amount [1, 2]. It is well known, that the special properties of poly(tetrafluorethene) are its high chemical, physical and fire resistance as well as high thermal stability which allow application temperature up to 533 K, low friction coefficient, good electrical insulator and little water adsorption etc. Their thermal endurance is related to the number of fluorine atoms in the repeating unit. Owing to the high strength of the C–H bond, PTFE is positioned at the top edge of the performances. It is a good electrical insulator, is difficult to burn, is highly antiadhesive and shows a low incorporation of water [2, 3]. Fluoropolymers, and especially the poly(tetrafluoroethene), are widely used in industry due to their special properties. They find industrial application in pipes and hoses, valves, thermocouple wells, gaskets, heat exchangers o-ring and dynamic seals, to name a few. The properties of PTFE are derived mainly from the strong carbon-fluorine bond energy of 507 kJ mol^{-1}, compared with typical energies of 415 kJ mol^{-1} for C–H or 348 kJ mol^{-1} for C–C bonds [1, 2, 4]. On these reasons, the practical applications of this polymer and its composites are very large in various fields of industry [1, 2, 4].

PTFE is non-melt-processible, hence one of the recycling methods is *via* thermolysis or pyrolysis of the solid waste and subsequent recovery of the monomer for re-use [2, 5]. Its continuous service temperature is 533 K and, for short periods, the polymer can withstand peak temperatures as high as 723 K without any appreciable weight loss. Slow decomposition of PTFE occurs above the application temperature of 533 K. However, for a noticeable decomposition to occur, temperatures above 673 K are needed. It has long been known that the thermal decomposition of PTFE predominantly yields tetrafluoroethene (TFE) and difluorocarbondiradicals (CF_2). Further products are formed by secondary reactions depending on temperature, reaction pressure and reaction atmosphere. The typical main products are (TFE) hexafluoropropene (HFP), octafluorocyclobutane (OFCB, c-C_4F_8) and other fluorocarbons [1, 2, 5, 6]. The product ratios can be tailored by manipulating the working temperature, the pressure, the residence time of the gaseous product stream in the hot zone, and the quench rate [5–7]. The product distribution was explained by a radical decomposition mechanism. Owing to the high bond energies of C–F bonds, C–C bonds were broken almost exclusively [1]. The produced radicals undergo an "unzip reaction" because the formation of TFE and a new radical is favored energetically Heavier substances like HFP, c-C_4F_8 or others are formed by secondary reactions, especially under higher pressures. A variety of reactions are possible in the thermal degradation of PTFE in inert atmosphere. According to Simon and Kaminsky [2], the degradation may be described by the following reactions:

(1) Radical formation/chain cleavage:

$$\begin{aligned}&R - CF_2 - CF_2 - CF_2 - CF_2^{\bullet} - R' \\ &\quad \rightarrow R - CF_2 - CF_2 - CF_2^{\bullet} + R' - CF_2^{\bullet} \qquad (I)\end{aligned}$$

(2) Monomer formation:

$$R - CF_2 - CF_2 - CF_2^{\bullet} \rightarrow R - CF_2^{\bullet} + CF_2 = CF_2 \qquad (II)$$

(3) Secondary reactions:

$$\begin{aligned}&2CF_2 = CF_2 \rightarrow {}^{\bullet}CF_2 - CF_2 - CF_2 - CF_2^{\bullet} \\ &\qquad \rightarrow c - C_4F_8 \qquad (III)\end{aligned}$$

$$2CF_2 = CF_2 \rightarrow CF_3 - CF = CF_2 + {}^{\bullet}CF_2^{\bullet} \qquad (IV)$$

$$CF_2 = CF_2 + {}^{\bullet}CF_2^{\bullet} \rightarrow CF_3 - CF = CF_2 \qquad (V)$$

The slowest reaction is the chain cleavage. This is the rate-determining step of the decomposition [2]. But reliable analysis and effective optimization of such processes need precise data on the characteristic temperature and kinetic parameters of the PTFE thermal decomposition at different conditions [4]. In this connection, for an adequate design and/or operation of the equipment involved in the recycling of PTFE by decomposition processes it is necessary to known the kinetics of the processes, that is to say, reaction rates. Knowledge of depolymerization kinetics is essential for reactor design and industrial scaling [5, 6]. On this reason the studies of thermal stability and degradation mechanism are very important and useful.

Kinetic analysis of thermal decomposition processes has been the subject interest for many investigators all along the modern history of thermal decomposition. The interest is fully justified. On one side, kinetic data are essential for describing any kind of device, in which the thermal decomposition takes place; on the other side, kinetics is intrinsically related whit the decomposition mechanism. The knowledge of the mechanism allows the postulation of kinetic equations or vice versa, and kinetics is the starting point to postulate mechanisms for the thermal decompositions [1, 2, 6, 8]. Knowledge of kinetic parameters, such as the reaction rate, activation energy and pre-exponent factor, is one of the keys to determine the reaction mechanism in the solid-state reactions. Practically, the kinetic triplet is needed to provide a mathematical description of the processes. If the kinetic triplet is determined correctly, it can be used to reproduce the original kinetic data as well as to predict the process kinetics outside the experimental temperature region [1, 9]. Thermogravimetric analysis (TGA) is one of the most commonly used technologies to study of a variety of primary reactions of decomposition of solids and estimate the kinetics parameters of these processes [1, 9, 10]. However, thermogravimetric studies of PTFE in oxidative atmosphere (combustion) or inert atmosphere (pyrolysis) are not so extensive, in spite of the information about incineration processes that can be obtained from this technique [1–3, 10, 11].

It is well known, that the determination of kinetic parameters by non-isothermal methods offers advantages over conventional isothermal studies. The conventional non-isothermal single scan method, which can not detect the complex nature of the solid-state reaction, has been replaced by multiple scan method at different heating rates using iso-conversional and iso-temperature calculation procedures [12–14]. Among the iso-conversional methods, Ozawa–Flynn–Wall (OFW) method [15–17], Kissinger–Akahira–Sunose (KAS) method [18, 19] and Popescu (P) method [20] have been widely used to estimate the activation energies E, pre-exponential factor A in Arrhenius equation and the most probable mechanism function $g(\alpha)$, knowing as a kinetics triplet of the processes. These methods are based on the assumption concerning the temperature integral, which will bring the homologous error.

In the present work simultaneous TG/DTA was used to determine the kinetics parameters and the most probable integral conversion function $g(\alpha)$ of non-isothermal oxidative degradation of PTFE, using iso-conversional calculation procedure.

Experimental

Material and Measurement

The samples of PTFE (Hostaflon) provided by Hoechest – Germany have been used in the experiments. It was used without further purification. The thermogravimetrical measurements were carried out in an air flow at a rate of 25 cm^3 min^{-1} under non-isothermal conditions on a MOM-Budapest derivatograph, system F. Paulik–I. Paulik–L. Erdey, which records T, TG, DTG and DTA curves simultaneously. Samples of 50 mg mass were used for the experiments varied out at hearing rates of 6, 10, 12 and 15 K min^{-1} up to 973 K. The samples were loaded without pressing into an open platinum crucible. α-Alumina calcined up to 1373 K was used as a standard reference material.

Mathematical background

Thermogravimetric analysis (TGA) is one of the most commonly used techniques to study the primary reactions of decomposition of solids. The kinetics of such reactions is described by various equations taking into account the special features of their mechanisms. The reaction rate can be expressed through the degree of conversion α according to the formula:

$$\alpha = \frac{m_i - m_t}{m_i - m_f}, \tag{1}$$

where: m_i, m_f and m_t are the initial, final and current sample mass at the moment t, respectively. Generally, the kinetic equation of the process can be written as follows [14]:

$$\mathrm{d}\alpha/\mathrm{d}t = \mathrm{k}(T)\mathrm{f}(\alpha) \tag{2}$$

The temperature dependence of the rate constant k for the process is described by the Arrhenius equation:

$$k = A\exp(-E/RT), \tag{3}$$

where: A is the pre-exponential factor, E is the apparent activation energy, T is the absolute temperature and R is the gas constant (8.314 J mol^{-1} K^{-1}). Substitution of Eq. 3 in Eq. 2 gives:

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = A\exp\left(-\frac{E}{RT}\right)\mathrm{f}(\alpha) \tag{4}$$

When the temperature increases at a constant rate,

$$\mathrm{d}T/\mathrm{d}t = q = \text{const}, \tag{5}$$

therefore:

$$\frac{\mathrm{d}\alpha}{\mathrm{d}T} = \frac{A}{q}\exp\left(-\frac{E}{RT}\right)\mathrm{f}(\alpha) \tag{6}$$

The differential conversion function f(α) for a solid-state reaction depends on the reaction mechanism and can generally be considered to be as follows [21]

$$\mathrm{f}(\alpha) = \alpha^{\mathrm{m}}(1-\alpha)^{\mathrm{n}}[-\ln(1-\alpha)]^{\mathrm{p}} \tag{7}$$

where: m, n and p are empirically obtained exponent factors, one of them always being zero. The combinations of different values of m, n and p make it possible to describe various probable mechanisms [21].

After substitution of Eq. 7 in Eq. 6, separation of variables and integration, the following general equation was obtained:

$$\int_0^{\alpha} \frac{\mathrm{d}\alpha}{\alpha^m(1-\alpha)^n[-\ln(1-\alpha)]^p} = \frac{A}{q}\int_0^T \exp\left(-\frac{E}{RT}\right)\mathrm{d}T \tag{8}$$

The solutions of the left hand side integral depend on the explicit expression of the differential conversion function f(α) and are denoted as g(α). The formal expressions of the integral conversion functions g(α) depend on the conversion mechanism and its mathematical model [14, 21–24]. The latter usually represents the limiting stage of the reaction – the chemical reactions; random nucleation and nuclei growth; phase boundary reaction or diffusion. Algebraic expressions of functions of the most common reaction mechanisms operating in solid-state reactions are presented in [14].

Several authors [15, 25, 26] suggested different ways to solve the right hand side integral. For the present study, one calculation procedure was based on Coats and Redfern equation [26]. Data from TG and DTG curves in the decomposition range $0.1 < \alpha < 0.9$ were used to determine the kinetic parameters of the process in all used calculation procedures. The integral method of Coats and Redfern has been mostly and successfully used for studying of the kinetics of dehydration, decomposition and combustion of different solid substances [8, 14]. The kinetic parameters can be derived using a linear form of modified Coats and Redfern equation:

$$\ln\frac{g(\alpha)}{T^2} = \ln\left[\frac{AR}{qE}\left(1-\frac{2RT}{E}\right)\right] - \frac{E}{RT} \cong \ln\frac{AR}{qE} - \frac{E}{RT} \tag{9}$$

If the correct g(α) function is used, a plot of $\ln[g(\alpha)/T^2]$ against $1/T$ should give a straight line from which the values of the activation energy E and the pre-exponential factor A in Arrhenius equation can be calculated.

Later, several authors [27–30] suggested different solutions of the temperature integral in Eq. 8, sustaining the opinion that this increases the precision of the kinetic parameters being calculated. For instance, Madhusudanan–Krishnan–Ninan [27, 28] suggested the following equation:

$$\ln\left[\frac{g(\alpha)}{T^{1.921503}}\right] = \left[\ln\frac{AE}{qR} + 3.772050 - 1.921503\ln E\right] - 0.120394\frac{E}{T}, \tag{10}$$

Tang et al. [29] suggested another kinetic equation:

$$\ln\left[\frac{g(\alpha)}{T^{1.894661}}\right] = \left[\ln\frac{AE}{qR} + 3.63504095 - 1.894661\ln E\right] - 1.00145033\frac{E}{RT} \tag{11}$$

and Wanjun et al. [31] suggested the equation:

$$\ln\left[\frac{g(\alpha)}{T^2}\right] = \ln\left[\frac{AR}{q\left(1.00198882E + 1.87391198RT_p\right)}\right] - \frac{E}{RT} \tag{12}$$

Equations 9–12 imply that there would be differences in the calculated values of the activation energy E and pre-exponential factor A even when the same $g(\alpha)$ function is used. To find which calculation procedure would turn out to be the most suitable for the calculations, they were estimated by the criterion "the best" correlation coefficient of the linear regression R^2 for Eqs. 9–12. The advantage of these equations is that the values of E and A can be calculated on the basis of single rate TG curves and the type of the most probable mechanism function of the studied reaction can be determined. For the calculations of the kinetic parameters a computer program was developed for all the data manipulations.

The second approach used for the calculations was based on multiple rates TG curves and so-called iso-conversional calculation procedures [15, 22, 31–34].

Calculation of activation energy by iterative procedure

To calculate the values of the activation energy of thermooxidative degradation of PTFE, first the Ozawa–Flynn–Wall (OFW) equation [15–17] was used:

$$\ln q = \ln\frac{0.0048AE}{g(\alpha)R} - 1.0516\frac{E}{RT} \tag{13}$$

and Kissinger–Akahira–Sunose (KAS) equation [18, 19]:

$$\ln\frac{q}{T^2} = \ln\frac{AR}{g(\alpha)E} - \frac{E}{RT} \tag{14}$$

These two methods of plotting a linear regressive curve were used at fraction conversion $0.1 < \alpha < 0.9$, and different heating rates q. The plots of $\ln q$ versus $1/T$ (Eq. 13) and $\ln(q/T^{2})$ versus $1/T$ (Eq. 14) have been proved to give the values of the apparent activation energy for the thermooxidative degradation of PTFE at different values of α. According these equations, the reaction mechanism and the shape of $g(\alpha)$ function cannot affect the calculation of the activation energy of the process. Iterative procedure was used to calculate the values of E approximating the exact value, according to the next equations [22, 32–34]:

$$\ln\frac{q}{H(x)} = \ln\frac{0.0048AE}{g(\alpha)R} - 1.0516\frac{E}{RT} \tag{15}$$

and

$$\ln\frac{q}{h(x)T^2} = \ln\frac{AR}{g(\alpha)E} - \frac{E}{RT}, \tag{16}$$

Since the right hand side integral in Eq. 8 has no exact analytical solution and, after making some variable substitution, it is expressed by the fourth Senum and Yang approximations [32, 35], which gives an accuracy better than $10^{-5}\%$ for $x = E/RT \geq 20$.

$$\frac{A}{q}\int_{o}^{T}\exp\left(-\frac{E}{RT}\right)\mathrm{d}T = \frac{AE\exp(-x)}{qR\quad x^2}h(x), \tag{17}$$

where: $h(x)$ is expressed by the fourth Senum and Yang approximation formulae [35]:

$$h(x) = \frac{x^4 + 18x^3 + 88x^2 + 96x}{x^4 + 20x^3 + 120x^2 + 240x + 120}, \tag{18}$$

where: $x = E/RT$ and $H(x)$ is equal to [22]:

$$H(x) = \frac{\exp(-x)h(x)/x^2}{0.0048\exp(-1.0516x)} \tag{19}$$

The iterative procedure performed involved the following steps: (i) Assume $h(x) = 1$ or $H(x) = 1$ to estimate the initial value of the activation energy E_1. The conventional iso-conversional methods stop the calculation at this step; (ii) using E_1, calculate a new value of E_2 for the activation energy from the plot of $\ln[q/H(x)]$ versus $1/T$ or $\ln[q/h(x)T^{2})$ versus $1/T$; (iii) repeat step (ii), replacing E_1 with E_2. When $E_\mathrm{i}–E_\mathrm{i-1} < 0.01$ kJ mol^{-1}, then the last value of E_i were considered to be the exact value of the activation energy of the studied reaction. These plots are model independent since the estimation of the apparent activation energy does not require selection of particular kinetic model (type of $g(\alpha)$ function). Therefore, the activation energy values obtained by this method are usually regarded as more reliable than these obtained by a single TG curve.

Determination of the most probably mechanism function

The following equation was used to estimate the most correct reaction mechanism, i.e. $g(\alpha)$ function [22]:

$$\ln[g(\alpha)] = \left[\ln\frac{AE}{R} + \ln\frac{e^{-x}}{x^2} + \ln h(x)\right] - \ln q \tag{20}$$

Plotting ln[g(α)] versus ln q and using a linear regressive of least square method, if the mechanism studied conforms to certain g(α) function, the slope of the straight line should be equal to -1.0000 and the linear correlation coefficient R^2 should be equal to unity. The values of E and A do not influence the shape of the most correct reaction mechanism function determined. For determination of the most probable mechanism function, the values of the conversion α corresponding to multiple rates taken at the same temperature were put into the left side of Eq. 20 and all the twenty-seven types of mechanism functions presented in [14] were tested. The slope and correlation coefficient were obtained from the plot of ln[g(α)] versus ln q. The most probable mechanism function was assumed to be the one for which the value of the slope of the straight line was closest to –1.0000 and the correlation coefficient was higher. If several g(α) functions comply with this requirement, the values of conversion α corresponding to multiple rates at the same temperature were applied to calculate the probable mechanism by the same method. Thus, the most probable mechanism function was considered to be the one for which the slope of the straight line was closest to –1.0000 and the linear correlation coefficient R^2 was near to unity.

Calculation of pre-exponential factor A in Arrhenius equation

The pre-exponential factor A can be estimated from the intercept of the plots of Eqs. 15 and 16, inserting the most probable g(α) function determined. All calculations were performed using a programs compiled by ourselves.

The values of the pre-exponential factor A in Arrhenius equation for solid phase reactions are expected to be in a wide range (six or eight orders of magnitude), even after the effect of surface area is taken into account [36, 37]. For first order reactions, the pre-exponential factor may vary from 10^5 to 10^{18} s^{-1}. The low factors will often indicate a surface reaction, but if the reactions are not dependent on surface area, the low factor may indicate a “tight” complex. The high factors will usually indicate a “loose” complex [36]. Even higher factors (after correction for surface area) can be obtained for complexes having free translation on the surface. Since the concentrations in solids are not controllable in many cases, it would have been convenient if the magnitude of the pre-exponential factor indicated for reaction molecularity. However, this appears to be true only for non-surface-controlled reactions having low ($<10^9$ s^{-1}) pre-exponential factors. Such reactions (if elementary) can only be bimolecular [36, 37].

Using Arrhenius equation (Eq. 3) we may be calculate the values of the rate constant k for every one temperature in the temperature interval in which process combustion of PTFE. From the theory of the activated complex (transition state) of Eyring [14, 36, 37], the following general equation may be written:

$$k = \frac{\chi k_{\mathrm{B}} T}{h} \exp\left(\frac{\Delta S^{\neq}}{R}\right) \exp\left(-\frac{\Delta H^{\neq}}{RT}\right), \tag{21}$$

where χ is the transmission coefficient, which is unity for monomolecular reactions; k_{B} is the Boltzmann constant, h is the Plank constant, $\Delta S^{\neq}$ and $\Delta H^{\neq}$ are the changes of entropy and enthalpy $\Delta H^{\neq}$ for the formation of the activated complex from the reagent respectively. Taking logarithms and rearranging we become:

$$\ln\frac{kh}{\chi k_B T} = \frac{\Delta S^{\neq}}{R} - \frac{\Delta H^{\neq}}{RT} \tag{22}$$

Plotting $\ln(kh/\chi k_{\mathrm{B}}T)$ versus $1/T$ and using a linear regressive of least square method, the values of the changes of entropy $\Delta S^{\neq}$ and enthalpy $\Delta H^{\neq}$ may be calculated from the intercept and the slope of the draw straight line respectively. Using the well known thermodynamic equation:

$$\Delta G^{\neq} = \Delta H^{\neq} - T_{\mathrm{P}} \Delta S^{\neq}, \tag{23}$$

the change of the Gibbs free energy $\Delta G^{\neq}$ for the activated complex formation from the reagent can be calculated. The values of $\Delta S^{\neq}$, $\Delta H^{\neq}$ and $\Delta G^{\neq}$ were calculated at $T = T_{\mathrm{P}}$ (T_{P} is the DTG peak temperature), since this temperature characterizes the highest rate of the process, and therefore, is its important parameter.

Results and discussion

Figure 1 shows the general shape of the pyrolysis and combustion TG curves for thermooxidative degradation of PTFE at four different heating rates.

As can be seen from Fig. 1 with increasing of the heating rate, the TG curves are shifted to the higher temperatures. One fact that must be emphasized is the high temperature of decomposition of this polymer (~873 K), compared with other polymers such as poly(ethene), poly(propene), poly(butadiene) and PVC. Another important fact is that the TG curves of combustion are very similar to those of pyrolysis, but the combustion takes place at lower temperatures [1].

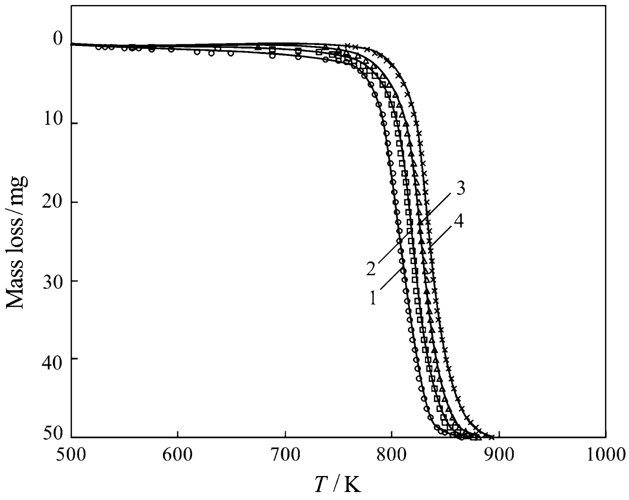
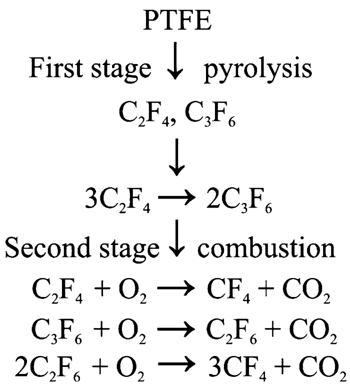


Fig. 1 Experimental TG curves for thermooxidative degradation of PTFE at heating rates: 1–6; 2–10; 3–12 and 4–15 K min^{-1}



Scheme 1 Reaction scheme for the thermal degradation of PTFE

On Fig. 2 are presented the kinetic curves, obtained according Coats–Redfern calculation procedure only for 10 K min^{-1} heating rate and using mechanism non-invoking kinetic equations with different values of n [see Ref. 14].

As can be seen for all the cases illustrated in Fig. 2, the kinetic curves bend at about 810 K. This was considered enough to conclude that the thermooxidative degradation of PTFE occurs in two stages described by different kinetic equations, which was confirmed also by the kinetic curves registered at the other three heating rates. According to Conesa and Font [1], the first stage is associated with pyrolysis of PTFE and the second stage—with combustion of the char formed. Garcia et al. [6] proposed the following scheme for the thermal PTFE degradation: (Scheme 1)

Using Coats – Redfern calculation procedure and the mechanism non-invoking equations with different values of n, the calculations for the first stage showed that straight lines with the highest correlation coefficient R^2 were obtained at $n = 1.75$, while for the second stage—at $n = 0.75$. Similar results have been reported by other authors [1, 4] who also stated that the thermooxidative degradation of PTFE occurs in two stages described by different kinetic equations and g(α) functions, respectively. To confirm this opinion, the iso-conversional calculation procedure of Ozawa–Flynn–Wall [15–17] was used. The corresponding lines obtained at different fraction conversion α and different heating rates q is presented in Fig. 3.

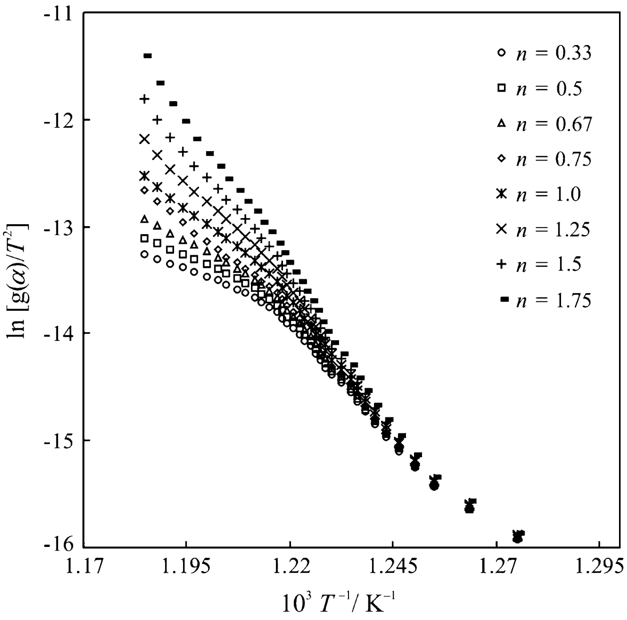


Fig. 2 Coats–Redfern plots for thermooxidative degradation of PTFE at heating rate 10 K min^{-1} using mechanism non-invoking equations with different values of n

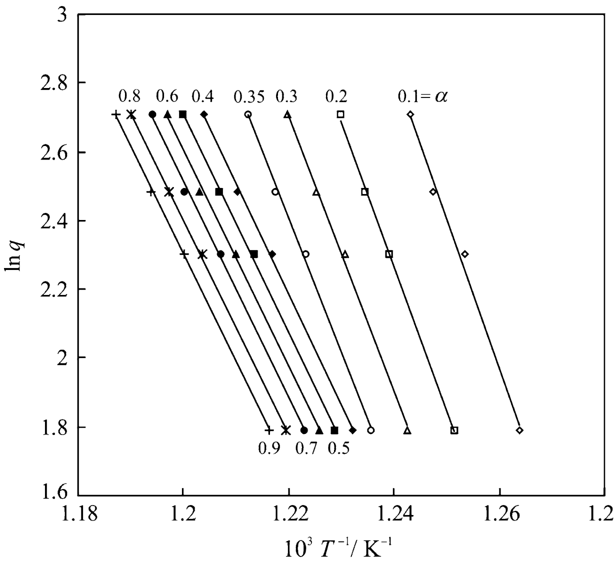


Fig. 3 Isoconversional plots at various conversion degrees for PTFE draw according OFW calculation procedure (Eq. 13)

It can be seen from Fig. 3 that two groups of straight lines are formed depending on the degree of conversion α: one with steeper lines and lower conversion degree ($\alpha < 0.35$) and the other—the lines of smaller slope and conversion degree $0.35 < \alpha < 0.9$. The same tendency was observed when the iso-conversional calculation procedure of Kissinger–Akahira–Sunose [18, 19], presented on Fig. 4 was used.

For comparison, the values of the activation energies of thermooxidative degradation of PTFE obtained according to OFW and KAS calculation procedures and Eqs. 15 and 16 are shown in Table 1.

As can be seen from the values presented in Table 1, the first stage of thermooxidative degradation of PTFE is characterized by significantly higher activation energies compared to the second stage. For the individual stages, the activation energies calculated according to the all four calculation procedures discussed are practically equal. Since these values do not depend on the type of the g(α) function, we used Eq. 20 to find the most probable mechanisms of the two stages. Plotting ln [$g(\alpha)$] versus ln q (Fig. 5) and using all twenty-seven types of mechanism functions presented in [14] and a linear regressive of least square method, the most probable shape of the g(α) function was determined.

If the mechanism studied conforms to certain g(α) function, the slope of the straight line should be equal to -1.0000 and the linear correlation coefficient R^2 should be equal to unity. It was found that values closest to unity can be obtained with different g(α) functions. For both stages, it was the mechanism non-invoking g(α) function with $n = 1.75$ for the first stage and $n = 0.75$ for the second stage, respectively. Knowing the most probable kinetic mechanism of the thermooxidative degradation of PTFE and using Coats–Redfern and Madhusudanan–Krishnan–Ninan calculation procedures, the corresponding lines for the first and second stages of thermal degradation of PTFE drew according Eqs. 9 and 10 are presented in Fig. 6.

For comparison, the values of the activation energy E and frequency factor A in Arrhenius equation, calculated from single TG curves at different heating rates and Coats–Redfern and Madhusudanan–Krishnan–Ninan calculation procedures, respectively, are presented in Table 2.

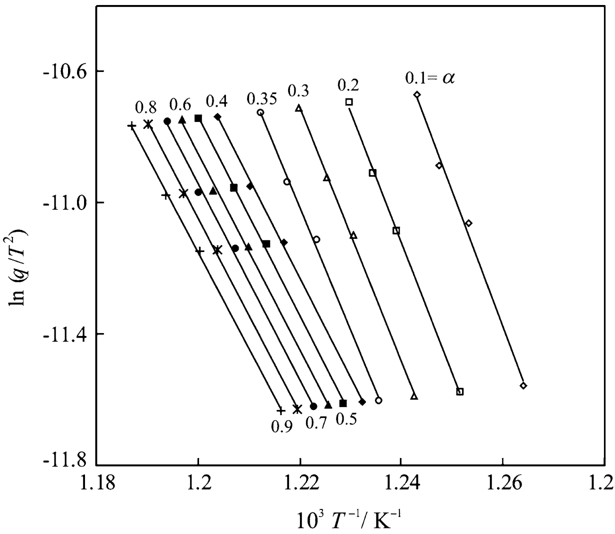


Fig. 4 Isoconversional plots at various conversion degrees for PTFE draw according KAS calculation procedure (Eq. 14)

Table 1 The activation energies for thermooxidative degradation of PTFE, E (kJ mol^{-1}), at different conversion degree and calculating procedure

Degree of decomp., α	OFW method	KAS method	ln [$q/H(x)$] ~ 1/T	ln [$q/h(x)T^2$] ~ 1/T
First stage (pyrolysis)				
0.1	341.4	345.7	345.7	345.9
0.2	330.3	333.9	333.9	334.2
0.3	318.4	321.3	321.4	321.6
0.35	306.7	309.0	309.1	309.3
Average	324.2	327.5	327.6	327.7
Second stage (combustion)				
0.4	253.5	253.0	253.3	253.3
0.5	252.0	251.8	252.2	252.2
0.6	249.4	248.5	248.9	248.8
0.7	248.6	247.7	248.1	248.1
0.8	246.5	245.5	245.9	245.8
0.9	245.8	244.7	245.1	245.1
Average	249.4	248.5	248.9	248.9

ln [$q/H(x)$] ~ 1/T is the iterative results of OFW method and ln [$q/h(x)T^2$] ~ 1/T is the iterative results of KAS method respectively

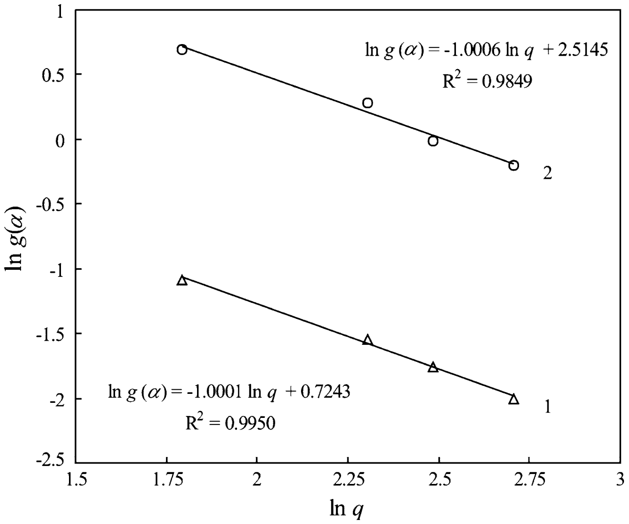


Fig. 5 Plots of ln $g(\alpha)$ versus ln q for thermooxidative degradation of PTFE: *1* first stage at $n = 1.75$ and *2* second stage at $n = 0.75$

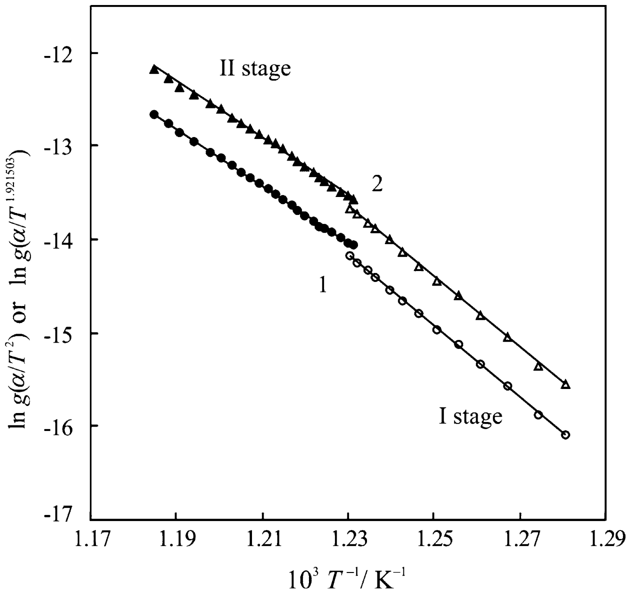


Fig. 6 Coats–Redfern (*1*) and Madhusudanan–Krishnan–Ninan (*2*) plots for thermooxidative degradation of PTFE at heating rate 10 K min^{-1} for I stage $n = 1.75$ and for II stage $n = 0.75$

Table 2 indicates that the values of E and A increased with the increase of heating rate and remain always higher for the first stage despite the calculation procedure used for both stages. Comparing the average values of the activation energy obtained by the methods of Coats–Redfern and Madhusudanan–Krishnan–Ninan (Table 2) with these obtained by the isoconversional calculation procedures (Table 1), the difference between them was found to be less than 5 kJ mol^{-1} for both stages. The values of E and A under the kinetic model found and g(α) selected were checked for correctness using the kinetic compensation effect, isokinetic effect, or θ-rule described with the following linear equation [11, 38–43] as criterion.

$$\ln A = \ln k_{iso} + \frac{E}{RT_{\mathrm{iso}}} \tag{24}$$

If a linear dependence between ln A and E is observed, then the isokinetic temperature T_{iso} and isokinetic rate constant k_{iso} may be calculated. The kinetic compensation effect for the both stages of thermal decomposition of PTFE, using the data obtained from Madhusudanan–Krishnan–Ninan calculation procedure is illustrated in Fig. 7.

As can be seen from Fig. 7, there is linear dependence between ln A and E for both stages, described by the following empiric equations:

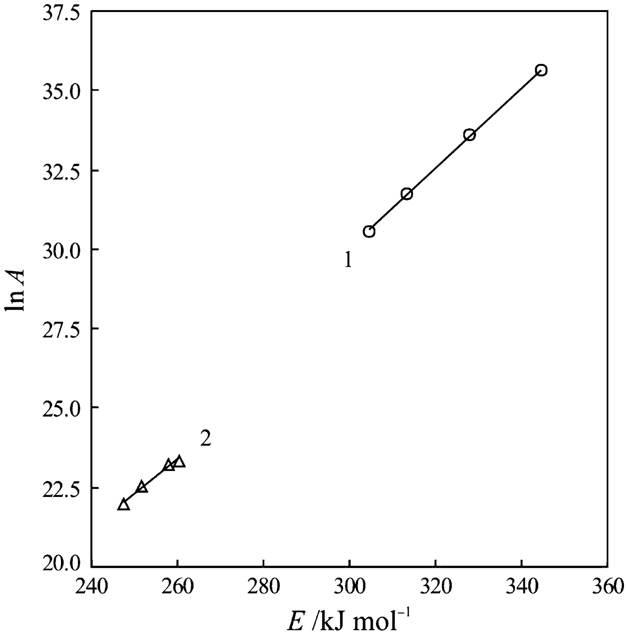


Fig. 7 Plot of kinetics compensation effect for: *1* I and *2* II stage

Table 2 Kinetic parameters of thermooxidative degradation of PTFE estimated by the single heating rate plots, calculated according Eqs. 9 and 10

Parameter	Coats–Redfern				Madhusudanan–Krishnan–Ninan			
q/K min^{-1}	6	10	12	15	6	10	12	15
I stage ($n = 1.75$)								
R^2	0.9820	0.9653	0.9856	0.9988	0.9821	0.9672	0.9856	0.9988
E/kJ mol^{-1}	304.4	313.3	327.6	344.2	304.6	313.5	327.8	344.4
A/min^{-1}	1.03×10^{19}	3.39×10^{19}	2.11×10^{20}	1.61×10^{21}	1.92×10^{13}	6.27×10^{13}	3.91×10^{14}	2.96×10^{15}
II stage ($n = 0.75$)								
R^2	0.9842	0.9671	0.9617	0.9130	0.9843	0.9654	0.9619	0.9133
E/kJ mol^{-1}	247.6	251.5	257.1	260.0	247.9	251.8	257.9	260.3
A/min^{-1}	1.80×10^{15}	3.27×10^{15}	6.43×10^{15}	7.24×10^{15}	3.41×10^{9}	6.18×10^{9}	1.22×10^{10}	1.37×10^{10}

$$\text{I stage} \quad \ln A = -7.8759 + 0.1264\,E \tag{25}$$

$$\text{II stage} \quad \ln A = -5.5011 + 0.1111\,E \tag{26}$$

Based on these equations, the values of the iso-kinetic rate constant k_{iso} (3.80×10^{-4} and 4.08×10^{-3} min^{-1}) and the iso-kinetic temperature T_{iso} (951.6 and 1082.6 K) for the first and the second stage, respectively, were calculated.

Using Eq. 22 and the data obtained from Madhusudanan–Krishnan–Ninan calculation procedure, the dependence between $\ln(kh/\chi k_{\mathrm{B}}T)$ and $1/T$ for the both stages of the thermooxidative degradation of PTFE is presented in Fig. 8.

From the slope of the corresponding straight lines are calculated the values of $\Delta H^{\neq}$ and from the cut-off of the ordinate axe—the values of $\Delta S^{\neq}$ for the both stages of the thermooxidative degradation of PTFE. In Table 3 are given the obtained kinetic parameters for the first and second stage of thermooxidative degradation of PTFE.

The change of Gibbs free energy $\Delta G^{\neq}$ reflects the total energy increase of the system at the approach of the reagents and the formation of the corresponding activated complex. According to the Eq. 23 this energy is influenced by two thermodynamic parameters—the changes of enthalpy $\Delta H^{\neq}$ and entropy $\Delta S^{\neq}$ of the activated complex formation. The change of activation enthalpy shows the energy differences between the activated complex and the reagents. If this difference is small, the formation of the activated complex is favored, because the potential energy barrier is low. The change of reaction entropy $\Delta S^{\neq}$ reflects how near the system is to its own thermodynamic equilibrium. Low reaction entropy means that the material has just passed through some kind of physical or chemical aging process, bringing it to a state near its own thermodynamic equilibrium. In this situation, the material shows little reactivity, increasing the time taken to form the activated complex. On the other hand, when high activation entropy values are observed, the material is far from its own thermodynamic equilibrium. In this case, the reactivity is high and the system can react faster to produce the activated complex, which resulted in the short reaction times observed [44]. According to [45], the negative values of $\Delta S^{\neq}$ indicate that the activated complex has a more ordered structure than the reactants and the reaction may be classify as “slow” [46].

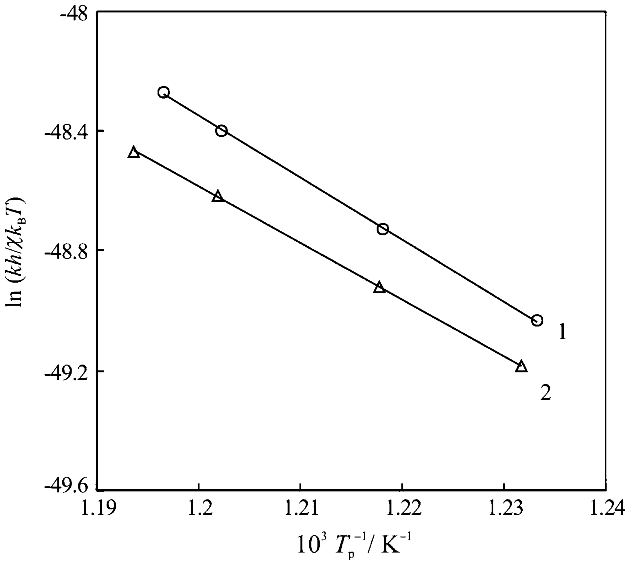


Fig. 8 Plot of ln ($kh/\chi k_{\mathrm{B}}T$) versus $1/T$ for: *1* I stage and *2* II stage of the thermooxidative degradation of PTFE

Conclusions

According to some authors [1, 4], pyrolysis and combustion of polymers, in particularly PTFE, including the simplest one, involve a great number of reactions. Thus, the pyrolysis is usually studied in terms of pseudo-mechanistic models. Depolymerization of polymers requires various processes: heating of the polymer, thermal decomposition (thermolysis, pyrolysis or combustion) connected with formation of different gaseous products and combustion of the char formation. Combustible and noncombustible gaseous decomposition products mix and react with air in the combustion zone above the surface, realizing heat during the production of carbon dioxide, water, and incomplete combustion products as carbon monoxide and soot. From a phenomenological point of view, the oxygen can also react with the polymer, producing a weight loss and volatile evolution different from the case of pyrolysis.

Based on the studies carried out, the thermooxidative degradation of PTFE occurs in two stages—pyrolysis and combustion, characterized by different values of the activation energy, pre-exponential factor in Arrhenius equation and thermodynamic parameters. These values strongly

Table 3 Most probably kinetics parameters of thermooxidative degradation of PTFE

Stage	n	E/kJ mol^{-1}	A/min^{-1}	$\Delta S^{\neq}$/J mol^{-1} K^{-1}	$\Delta G^{\neq}$/kJ mol^{-1}	$\Delta H^{\neq}$/kJ mol^{-1}
First	1.75	313.3	3.39×10^{19}	–84.8	242.6	173.0
Second	0.75	251.5	3.27×10^{15}	–96.9	244.2	164.7

depend on the shape of the correctly determined most probable mechanism function g(α) and calculation procedure used.

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