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KINETIC OF THERMAL DEGRADATION OF LOW-DENSITY AND HIGH-DENSITY POLYETHYLENE BY NON-ISOTHERMAL THERMOGRAVIMETRY

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Study of the decomposition kinetics is an important tool for the development of polymer recycling in industrial scale. In this work, parameters such as activation energy, frequency factor and reaction order, were measured under dynamic conditions. Flynn–Wall–Ozawa, Van Krevelen, Horowitz–Metzger, Coats–Redfern, Madhusudanan and Vyazovkin methods were used to determine the kinetic parameters. The analysis of the results obtained by the Coats–Redfern method shows that the thermal degradation process of LDPE and HDPE corresponds to a phase boundary controlled reaction (mechanism R2). This method shows that the reaction order values of LDPE and HDPE are about 0.7 and 0.6, respectively.

Keywords: *HDPE, kinetic analysis, LDPE, thermal degradation*

Introduction

Thermal degradation of polymers has great interest as an alternative source of energy or chemical raw materials, as well as it contributes to the solution of environmental problems [1]. The determination of the parameters of the thermal decomposition process by means of thermogravimetric techniques allows the development of the recycling process of these materials in an industrial scale. The properties and thermal degradation mechanism of polymers such as low-density and high-density polyethylene, are reasonably well known. Bockhorn [2] demonstrated that the thermodegradation of these polymers occurs through a random radical chain mechanism initiated by a homolytic scission reaction (I), followed by β-scission propagation reactions (II) and radical reactions leading to the formation of dienes and alkenes (III). Reaction (IV) leads to the formation of alkanes via the intermolecular hydrogen transfer of primary radicals and thus more stable secondary radicals are produced. At the end, a termination reaction is assumed via combination (V):

Initiation

$$\mathrm{R{-}(CH_2)_4{-}CH_2{-}R \xrightarrow{k_1} R{-}(CH_2)_4{-}CH_2{\bullet}+R{\bullet}} \tag{I}$$

β-scission propagation

$$\mathrm{R{-}(CH_2)_4{-}CH_2{\bullet} \xrightarrow{k_2} R{-}(CH_2)_2{-}CH_2{\bullet}+CH_2{=}CH_2} \tag{II}$$

Random propagation

$$\mathrm{R{-}(CH_2)_4{-}CH_2{\bullet} \xrightarrow{k_3} CH_3{-}(CH_2)_2{-}CH{=}CH_2+R{\bullet}} \tag{III}$$

Intermolecular hydrogen transfer

$$\mathrm{R{-}(CH_2)_4{-}CH_2{\bullet}+R{-}(CH_2)_2{-}CH_2{-}R \xrightarrow{k_4} R{-}(CH_2)_4{-}CH_3+R{-}CH_2{-}CH{-}CH_2{-}R{\bullet}} \tag{IV}$$

Termination

$$\mathrm{R{\bullet}+R{\bullet} \xrightarrow{k_5} R{-}R} \tag{V}$$

In this work, the evaluation of the kinetic parameters (activation energy, frequency factor and reaction order) the thermal degradation of low-density polyethylene (LDPE) and high-density polyethylene HDPE were carried out, using the integral and approximation methods under dynamic heating. The mechanisms of these solid-state reactions were also determined.

Experimental

Materials

The LDPE and HDPE sample (industrial degree) without inorganic additives, were obtained from Brazilian industries in the form of granules (pellets). The thermal degradation of all polymers were carried out using a thermobalance (Shimadzu TGA-50), in alu-

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mina pans at a heating rates of 5, 10 and 20ºC min^{-1}, from ambient temperature to 900°C under a steady flow of nitrogen (flow rate 50 mL min^{-1}), while the initial sample mass was 5.0±0.5 mg.

Modeling of degradation kinetics

A model for kinetic decomposition process is usually based on Eq. (1) [3]:

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t}=k(T)f(\alpha) \tag{1}$$

where t is time, T is temperature, α is the extent of conversion, and $f(\alpha)$ is the reaction model.

The temperature dependence of the kinetic constant (k) can be expressed by an Arrhenius expression:

$$k(T)=A\mathrm{e}^{\left(\frac{-\Delta \mathrm{E}}{\mathrm{RT}}\right)} \tag{2}$$

where A is the frequency factor, ΔE is the activation energy, R is the gas constant and T is the reaction temperature.

The reaction model $f(\alpha)$ is expressed as a function of the concentration of the reactive material available,

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t}=A_0\mathrm{e}^{\left(\frac{-\Delta \mathrm{E}}{\mathrm{RT}}\right)}(1-\alpha)^{\mathrm{n}} \tag{3}$$

where $(1-\alpha)$ is the amount of the remaining reactive polymer (dimensionless) and n is the reaction order [3].

Flynn–Wall–Ozawa method (FWO)

This method is based on the mass loss at different heating rates. Equation (3) can be presented as follows [4]:

$$\frac{\mathrm{d}\alpha}{(1-\alpha)^{\mathrm{n}}}=\frac{A}{\beta}\mathrm{e}^{\frac{-\Delta \mathrm{E}}{\mathrm{RT}}}\mathrm{d}T \tag{4}$$

it can be integrated from the initial condition of $\alpha=0$ at $T=T_0$ to obtain the following expression:

$$F(\alpha)=\int_0^{\alpha}\frac{\mathrm{d}\alpha}{(1-\alpha)^{\mathrm{n}}}=\frac{A}{\beta}\int_{\mathrm{T}_0}^{\mathrm{T}}\mathrm{e}^{\left(\frac{-\Delta \mathrm{E}}{\mathrm{RT}}\right)}\mathrm{d}T \tag{5}$$

Van Krevelen method (VK)

In the Van Krevelen method, a temperature $T_{\max}$ is where the rate is maximal and determined from the peak of the DTA curve. For the temperature range between $0.9T_{\max}<T<1.1T_{\max}$, the following approximation can be assumed [5, 6]:

$$\ln\{F(\alpha)\}=\ln\left[\frac{A}{\beta}\left(\frac{0.368}{T_{\max}}\right)^{\frac{\Delta \mathrm{E}}{\mathrm{RT_{max}}}}\left(\frac{1}{\frac{\Delta E}{RT_{\max}}+1}\right)\right]+ \\ +\left(\frac{\Delta E}{RT_{\max}}+1\right)\ln T \tag{6}$$

A plot of $\ln\{F(\alpha)\}$ *vs*. $\ln T$ should yield a slope, from which an activation energy can be calculated. This method requires only the relative mass of the sample, as a function of reaction temperature to determine the activation energy of the reaction.

Horowitz–Metzger method (HM)

An alternative method for calculating activation energies according to the best linear plot is proposed by Horowitz–Metzger [5, 7], which is used an approximate integration of the rate equation. In this method, $-\ln(1-\alpha)$ is plotted *vs*. β, resulting a straight line which slope is $\Delta E/RT$. The activation energy is calculated from the slope as follows:

$$\ln\left[\frac{1-(1-\alpha)^{1-\mathrm{n}}}{1-n}\right]=\frac{\Delta E\beta}{RT_{\mathrm{S}}} \tag{7}$$

where T_{s} is the peak temperature of the DTG curve.

Coats–Redfern method (CR)

The Coats–Redfern method is an integral method involving the mechanism of thermal degradation. Using an asymptotic approximation for the resolution of Eq. (5), can be obtained Eq. (8) [8, 9]:

$$\ln\frac{F(\alpha)}{T^2}=\ln\frac{AR}{\beta\Delta E}-\frac{\Delta E}{RT} \tag{8}$$

The expressions of $F(\alpha)$ for different mechanism were presented in Table 1, and the activation energy for each degradation mechanism can be obtained from the slope of the plot of $\ln[F(\alpha)/T_2]$ *vs*. $1000/T$.

Madhusudanan method (MD)

Another integral method is to evaluate a kinetic model was developed by Madhusudanan [10], to estimate the kinetic parameters from TG/DTG curves. The activation energy can be calculated from the following expression:

$$\ln\left[\frac{1-\ln(1-\alpha)}{T^{1.9206}(1-n)}\right]= \\ =\ln\frac{AR}{\beta R}+0.02-1.9206\ln\frac{\Delta E}{R}-0.12040\frac{\Delta E}{RT} \tag{9}$$

Table 1 Kinetic parameters of decomposition of LDPE and HDPE

Polymer	Kinetic model	β/°C min^{-1}	n	ΔE/kJ mol^{-1}	A/s^{-1}	r
LDPE	CR	5	0.12	126.09	$1.6\cdot10^{6}$	0.9998
		10	0.74	212.65	$2.8\cdot10^{12}$	0.9994
		20	0.66	235.19	$8.5\cdot10^{13}$	1.0000
	MD	5	0.81	228.42	$4.1\cdot10^{13}$	0.9988
		10	0.72	210.19	$1.9\cdot10^{12}$	0.9994
		20	0.65	234.59	$8.1\cdot10^{14}$	0.9999
	HM	5	0.84	252.07	$1.6\cdot10^{15}$	0.9991
		10	0.79	238.07	$1.6\cdot10^{14}$	0.9997
		20	0.89	275.81	$6.4\cdot10^{16}$	0.9999
	VK	5	0.82	238.18	$1.1\cdot10^{20}$	0.9968
		10	0.78	226.49	$1.5\cdot10^{19}$	0.9976
		20	0.75	247.40	$3.6\cdot10^{20}$	0.9894
HDPE	CR	5	0.60	202.36	$3.6\cdot10^{11}$	0.9990
		10	0.41	208.27	$9.8\cdot10^{11}$	1.0000
		20	0.62	247.44	$5.1\cdot10^{14}$	0.9996
	MD	5	0.62	204.57	$5.7\cdot10^{11}$	0.9990
		10	0.54	223.58	$1.4\cdot10^{6}$	0.9999
		20	0.50	238.41	$1.2\cdot10^{14}$	0.9997
	HM	5	0.65	227.33	$2.4\cdot10^{13}$	0.9994
		10	0.64	246.31	$5.7\cdot10^{14}$	0.9999
		20	0.62	269.04	$1.8\cdot10^{16}$	0.9998
	VK	5	0.62	213.62	$1.3\cdot10^{18}$	0.9981
		10	0.60	239.67	$1.0\cdot10^{20}$	0.9838
		20	0.53	249.64	$4.1\cdot10^{20}$	0.9950

The plot of the left side of the equation *vs.* the reciprocal of the absolute temperature yields a straight line. ΔE and A can be calculated from the slope and the intercept.

Vyazovkin method (VZK)

This method is based on the isoconversional method at multiple heating rates. Taking Eq. (5), and assuming that $\Delta E/2T>>1$, the temperature integral can be approximated by:

$$\int_{T_0}^{T} e^{\left(\frac{-\Delta E}{RT}\right)} dT \cong \frac{R}{\Delta E} T^{2} e^{\left(\frac{-\Delta E}{RT}\right)} \qquad (10)$$

Substituting the whole temperature, and applying logarithm operation, one obtains:

$$\ln\frac{\beta}{T^{2}} = \ln\left[\frac{Rk_0}{\Delta E F(\alpha)}\right] - \frac{\Delta E}{R}\frac{1}{t} \qquad (11)$$

This is defined as dynamic equation, which is used for the determination of the activation energy for all conversion values [11].

Results and discussion

Figure 1 illustrates the TG curves of LDPE and HDPE for the polyethylene samples heated in nitrogen atmosphere at various heating rates. It was found that the curves were displaced to higher temperatures due to the heat transfer lag with increasing heating rates.

The kinetic parameters were calculated using the CR, MD, HM and VK methods. Their respective linear regression coefficients (r), for both the polymeric types (LDPE and HDPE) and the different methods are presented in Table 1.

It can be observed that the activation energies of the thermal degradation of both types of polyethylene are not much affected by the heating rates. It was also observed that there is not a clear influence of the branching of the polymer chain on the kinetic parameters.

Since, the determination of kinetic parameters from only one TG curve involves linear regression techniques of low reliability, kinetic models with multiple heating rates, as described by Flynn–Wall–Ozawa and Vyazovkin, have been used (Table 2). Another reason for the use of the method proposed by Vyazovkin originates from the fact that in this method

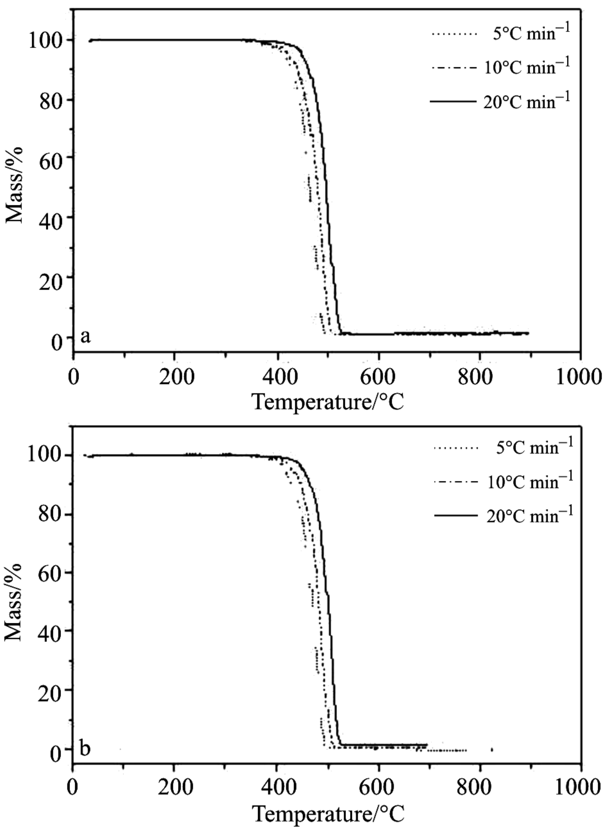

Fig. 1 TG Curves for a – LDPE and b – HDPE sample at different heating rates

is not necessary to select one value for the conversion function $f(\alpha)$, which makes possible a better accuracy in the study of the process of random scission of the chains in the polyethylenes.

Utilizing the activation energy values obtained by VZK method, the life time of polymers at different temperatures were evaluated (Fig. 2). For LDPE to obtain 50, 75 and 90% of thermal degradation in 300 min the necessary temperature are 390, 394 and 400ºC, respectively. Whereas to reach the same extent of decomposition 400, 404 and 433ºC temperatures are required for HDPE.

The activation energy values obtained by VK, HM, CR, MD, FWO and VZK methods for LDPE and HDPE are very close together. However there is a little discrepancy in the FWO method for the first one polymer, probably due to the utilization of Doyle's approximation in the integration of model, and another discrepancy was noticed upon using the Vyazovkin method for HDPE.

Generally, the activation energy values calculated for both polyolefins, LDPE and HDPE, are very close to the values reported in [12]. Small differences between the values are reported in this work and the literature data can be ascribed to the slightly different sample properties (e.g. purity, molecular mass), the method to measure the mass loss behavior during the polymer decomposition and the way of evaluation way of the kinetic parameters.

Determination of the reaction mechanism

Despite a great amount of works has dealt with kinetics of thermal decomposition of polyolefins in the recent years, the kinetic parameters reported vary widely from one publication to another [13, 14]. Thus, in this work, the use of the CR method is due to its wide applicability in the thermal decomposition of polymeric materials, as well as, to the good correlation between the experimental data and the data reported in literature.

Table 2 Activation energy of LDPE and HDPE by Flynn–Wall–Ozawa and Vyazovkin

Conversion (α)	FWO		VZK	
	LDPE	HDPE	LDPE	HDPE
	ΔE/kJ mol^{-1}			
10	164.95	162.49	251.71	296.53
20	179.10	181.15	259.98	292.61
30	185.67	190.79	259.72	290.98
40	191.28	199.58	257.06	288.13
50	195.39	205.59	251.13	293.37
60	200.29	210.83	250.21	293.05
70	204.00	216.62	248.97	283.29
80	205.35	224.62	238.06	279.60
90	206.71	230.48	–	–
average	192.53	202.46	251.56	290.54
sd	13.94	21.65	8.84	5.00

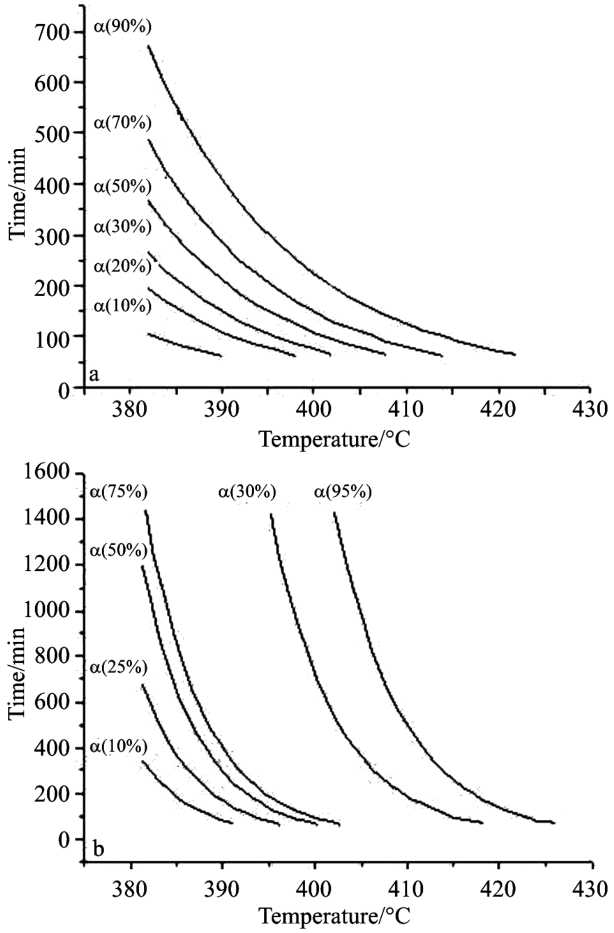

Fig. 2 Conversion time *vs*. temperature curves of a – LDPE and b – HDPE

According to Eq. (8), the activation energies for each $F(\alpha)$ function can be calculated at the constant heating rates using from the fitting of $\ln(F(\alpha)/T^2)$ *vs*. $1000/T$ plots. In order to determine which degradation mechanism of LDPE and HDPE are in the best agreement with the data, the obtained activation energies were compared. In Tables 3 and 4 the activation energies for the different decomposition mechanisms proposed using the heating rates of 5, 10 and 20ºC min^{-1} are summarized.

As the values of the correlation coefficients of the aforementioned mechanisms presented approximate values, the identification of the mechanism of thermal decompositon reaction in the solid state was carried out by the comparison of the fits between the theoretical and experimental data.

By comparison of the results with the values obtained by the Coats–Redfern method shows that the mechanism which best describes the thermal decomposition of LDPE and HDPE corresponding to the mechanism R2 (phase boundary controlled reaction – contracting area), for different heating rates. This was confirmed by the very good agreement between the experimental and non-isothermal data, as can be observed in Fig. 3. Thus, the rate of degradation of polymers is controlled by instantaneous processes of bidimensional nucleation and diffusion of the reagents through the products.

Table 3 Activation energy and decomposition mechanism of LDPE obtained by Coats–Redfern method

Mechanism	5ºC min^{-1}		10ºC min^{-1}		20ºC min^{-1}	
	ΔE/kJ mol^{-1}	r	ΔE/kJ mol^{-1}	r	ΔE/kJ mol^{-1}	r
A2	119.47	0.9985	115.47	0.9982	136.07	0.9988
A3	77.59	0.9985	74.92	0.9982	88.60	0.9989
A4	56.68	0.9985	54.65	0.9982	64.86	0.9989
D1	370.80	0.9960	358.98	0.9965	417.87	0.9942
D2	406.60	0.9994	393.36	0.9956	458.89	0.9998
D3	449.68	0.9998	435.52	0.9997	509.40	0.9998
D4	420.58	0.9999	407.27	0.9995	475.51	0.9996
F1	244.92	0.9985	237.13	0.9982	278.47	0.9988
F2	139.68	0.9063	135.48	0.9039	163.76	0.9076
F3	285.42	0.9062	277.14	0.9038	333.56	0.9017
P2	119.43	0.9920	115.47	0.9929	136.07	0.9884
P3	56.74	0.9920	54.68	0.9928	64.35	0.9883
R1	182.37	0.9921	176.40	0.9929	205.76	0.9885
R2	126.09	0.9998	212.65	0.9994	235.19	0.9995
R3	221.80	0.9996	214.47	0.9994	251.23	0.9997

Table 4 Activation energy and decomposition mechanism of HDPE obtained by Coats–Redfern method

Mechanism	5ºC min^{-1}		10ºC min^{-1}		20ºC min^{-1}	
	ΔE/kJ mol^{-1}	r	ΔE/kJ mol^{-1}	r	ΔE/kJ mol^{-1}	r
A2	115.67	0.9965	126.84	0.9982	143.61	0.9967
A3	75.08	0.9965	82.48	0.9982	93.62	0.9967
A4	54.79	0.9965	60.30	0.9982	68.63	0.9967
D1	361.55	0.9982	391.82	0.9962	445.68	0.9981
D2	395.47	0.9997	429.77	0.9995	487.64	0.9998
D3	436.90	0.9987	476.35	0.9996	538.93	0.9988
D4	409.15	0.9996	445.14	0.9999	504.67	0.9997
F1	237.44	0.9965	259.89	0.9982	293.58	0.9967
F2	132.77	0.8941	150.38	0.9051	165.66	0.8964
F3	271.63	0.8940	306.98	0.9050	337.68	0.8963
P2	115.67	0.9964	126.84	0.9924	143.61	0.9963
P3	55.17	0.9964	60.12	0.9924	68.98	0.9963
R1	177.72	0.9964	192.80	0.9924	219.66	0.9963
R2	202.36	0.9990	208.27	0.9909	247.44	0.9996
R3	215.40	0.9974	235.07	0.9993	266.28	0.9978

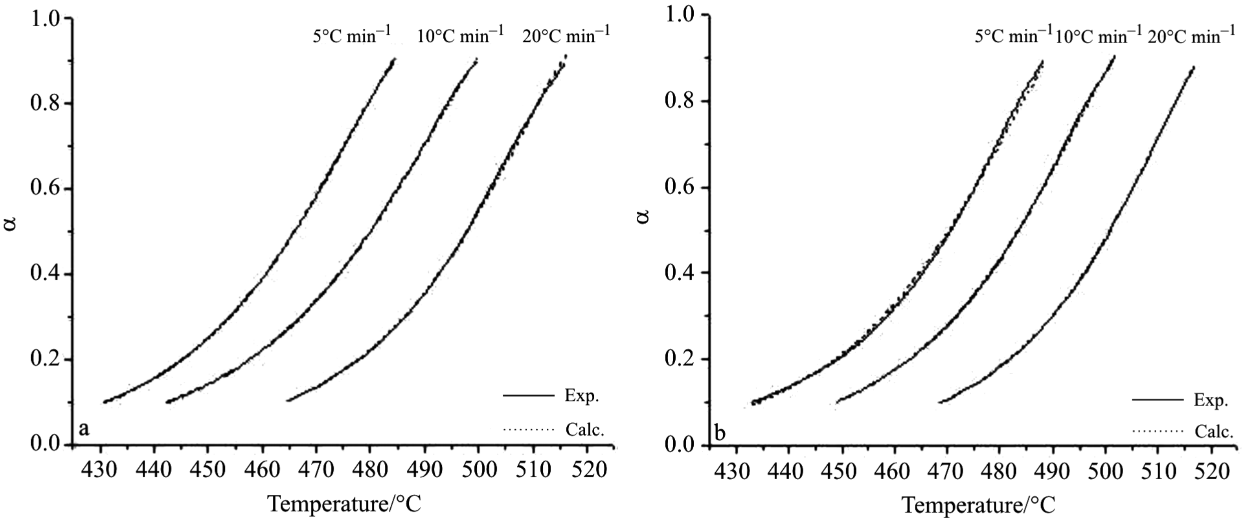

Fig. 3 Experimental and calculated conversion values for a – LDPE and b – HDPE at several temperatures by the thermal decomposition mechanism R2

Conclusions

The thermal degradation of both LDPE and HDPE was investigated under non-isothermal conditions. The kinetic parameters obtained by the integral and approximation methods presented a certain differences between them, mainly in the methods that use multiple heating rates. The analysis of the results obtained by Coats–Redfern method shows that the model which best describes the process of thermal decomposition reaction in solid-state for both polymers was R2.

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