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NON-ISOTHERMAL KINETICS OF DEGRADATION OF ULTRA-HIGH MOLECULAR MASS POLYETHENE COMPOSITE MATERIALS
Part I. Composite materials with fiber monocrystals

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In the present work, the Coats-Redfern method was used to determine the kinetic parameters and the possible reaction mechanism of the thermal degradation of ultra-high molecular mass polyethene and its composites with fiber monocrystals in static air at three different heating rates – 6, 10 and 16 K min^{-1}. The analysis of the results obtained showed that the thermal degradation process of pure ultra-high molecular mass polyethene corresponded to a diffusion controlled reaction (three-dimentional diffusion, mechanism D_3), while its composites with fiber monocrystals degraded by two concurrent mechanisms (diffusion one D_3 and A_1,F_1 mechanism). The fiber monocrystals used increased the thermal stability of the composite materials obtained. The values of the activation energy, frequency factor, the changes of entropy, enthalpy and Gibbs energy for the active complex of the composites were calculated.

Keywords: *composite materials, fiber monocrystals, kinetic parameters, ultra-high molecular mass polyethene*

Introduction

Polymer degradation of different polymers and composite materials (CM) based on them is known to be a very complex phenomenon comprising several elementary reactions which are difficult to analyze separately and their quantitative contribution to the global degradation process is virtually impossible to assess. This is the reason why mathematical models are developed. A mathematical model for thermal decomposition reactions is useful for the understanding and verification of the validity of the assumptions implied by such reactions.

Data on the mechanism and kinetics and mechanism of polymers thermal degradation can be obtained from the TG-curves recorded under dynamic heating conditions. To achieve the proposed goal, it is necessary to use different mathematical methods which can be used to predict the various kinetic parameters. These methods are: Horowitz–Metzger [1], Coats–Redfern [2], McCallum–Tanner [3], Mahusudanan–Krishnan–Ninan [4, 5], Dharwadkar and Karkhanavala [6], Reich Stivala [7], classic differential model [8], analytical method [8], etc.

Despite of the great efforts devoted to the kinetics of thermal decomposition of polyolefins in the recent years, the authors could not find publications for ultra-high molecular mass polyethene (UHMWPE) and composites based on it. Some authors have reported for experiments with low density polyethylene (LDPE) and high density polyethene (HDPE) and some composites based on them but the values of the kinetic parameters vary widely from one publication to another [9–11]. According to Sinfronio *et al.* [9], the results obtained by the Coats–Redfern method showed that the model which best describes the process of thermal decomposition reaction in solid state LDPE and HDPE was R_2 mechanism (phase boundary reaction), with activation energy HDPE degradation at heating rates of 5, 10 and 20 K min^{-1} in steady flow of nitrogen being 202.36; 208.27 and 247.44 kJ mol^{-1}, respectively. Other authors used the dynamic method [10]. The values of the activation energy of thermal destruction had been found to be 333.2–343.2 for HDPE and 187.5–199.1 kJ mol^{-1} for LDPE. Yet another publication on the activation energy of thermal degradation of HDPE in nitrogen medium determined by the Flynn and Wall methods, reported values of (238.4±3.7 kJ mol^{-1}).

Therefore, the aim of the present work is to determine the probable mechanism of thermal degradation of UHMWPE and its composites with fiber monocrystals and the corresponding values of the kinetic parameters.

Experimental

Materials

UHMWPE with melt index 0.001 g/10 min (temperature 463 K, load 21 kg) and molecular mass 1.8.10^6 was

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used, product of Lukoil Neftochim Bourgas Co. Fiber monocrystals (FMC) were synthesized by pyrolysis of alkali titanates containing 14.51% K_2O and 85.49% TiO_2 (Kharkov Polytechnical Institute, Ukraine). Their aspect ratio was 100, and the amount used in the composite materials ranged from 0 to 6 mass%.

The homogenization and preparation of the composites based on UHMWPE with FMC have been described earlier [12]. The mass loss and the thermal properties of the CM obtained were measured using OD-102 derivatograph (Hungary) in static air under three different heating rates 6, 10 and 16 K min^{-1}. Alumina crucibles were used with an initial sample mass of 50±1 mg.

The diameter of the single FMC fibers and their length were determined on a scanning electron microscope BS 380 TESLA (Czech Republic) under regime of secondary electrons at acceleration of 20 kV.

Modeling of degradation kinetics

The analyses of the thermal degradation kinetics of polyethylene and polyethylene composites were based on TG results. In TG measurements, the degree of transformation (α) is defined as:

$$\alpha=\frac{W_\mathrm{i}-W_\tau}{W_\mathrm{i}-W_\mathrm{f}} \tag{1}$$

where W_i, W_τ and W_f are the initial, actual and final mass of the sample, respectively. The degradation kinetic model can be expressed simply in the following general form [13]:

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

where $f(\alpha)$ is a function, the type of which depends on the reaction mechanism, $k(T)$ – the temperature dependent rate constant, T – the absolute temperature, τ – the time and α – the degree of transformation.

The temperature dependence of the rate constant k can be expressed by the Arrhenius equation [14]:

$$k=A\exp(-E_\mathrm{a}/RT) \tag{3}$$

where A is pre-exponential or frequency factor, R – the universal gas constant (8.314 J mol^{-1} K^{-1}) and E_a – the activation energy.

The combination of Eqs (2) and (3) gives the following equation:

$$\mathrm{d}\alpha/\mathrm{d}\tau=A\exp(-E/RT)f(\alpha) \tag{4}$$

Equation (4) is normally the fundamental basis for the kinetic analysis of a solid material from non-isothermal TG experimental data. Under constant heating rate

$$\mathrm{d}T/\mathrm{d}\tau=q=\text{const}$$

and, after substitution in Eq. (4) and some transformations, we obtain:

$$\int_0^\alpha\frac{d\alpha}{f(\alpha)}=\frac{A}{q}\int_0^\mathrm{T}\exp\left(\frac{E_\mathrm{a}}{RT}\right)\mathrm{d}T \tag{5}$$

If the solution of integral on the left-hand-side of Eq. (5) is denoted with

$$g(\alpha)=\int_0^\alpha\frac{d\alpha}{f(\alpha)} \tag{6}$$

then:

$$g(\alpha)=\frac{A}{q}\int_0^\mathrm{T}\exp\left(\frac{E_\mathrm{a}}{RT}\right)\mathrm{d}T \tag{7}$$

Method of Coats-Redfern

The Coats-Redfern method is an integral method, involving the mechanism of thermal degradation [2].

Substituting $x=E_\mathrm{a}/RT$ in Eq. (7) and after integration:

$$g(\alpha)=\frac{ART^2}{qE_\mathrm{a}}\left[1-\frac{2RT}{E_\mathrm{a}}\right]\exp\left(\frac{E_\mathrm{a}}{RT}\right) \tag{8}$$

Dividing both sides by T^2 taking the logarithms, Eq. (8) is transformed to:

$$\ln\frac{g(\alpha)}{T^2}=\ln\frac{AR}{qE_\mathrm{a}}\left(1-\frac{2RT}{E_\mathrm{a}}\right)-\frac{E_\mathrm{a}}{RT} \tag{9}$$

Since 2RT/Ea « 1 [2, 15], then:

$$\ln\frac{g(\alpha)}{T^2}=\ln\frac{AR}{qE_\mathrm{a}}-\frac{E_\mathrm{a}}{RT} \tag{10}$$

According to Eq. (10), the activation energies (E_a) and pre-exponential or frequency factors (A) for each $g(\alpha)$ function can be calculated at the constant heating rate using from the fitting of $\ln\frac{g(\alpha)}{T^2}$ *vs.* $1/T$ plots. If the correct $g(\alpha)$ function is used, the plot of $\ln\frac{g(\alpha)}{T^2}$ *vs.* $1/T$ should give a straight line with high correlation coefficient of the regression analysis.

The algebraic expressions of the functions in differential and integral form often used for thermal degradation during reactions in solid state [$f(\alpha)$ and $g(\alpha)$], depending on the kinetic model, are reported in [16].

In the present work, the kinetic parameters (E_a and A) were calculated by the Coats–Redfern method due to its wide applicability in the thermal decomposition of polymeric materials.

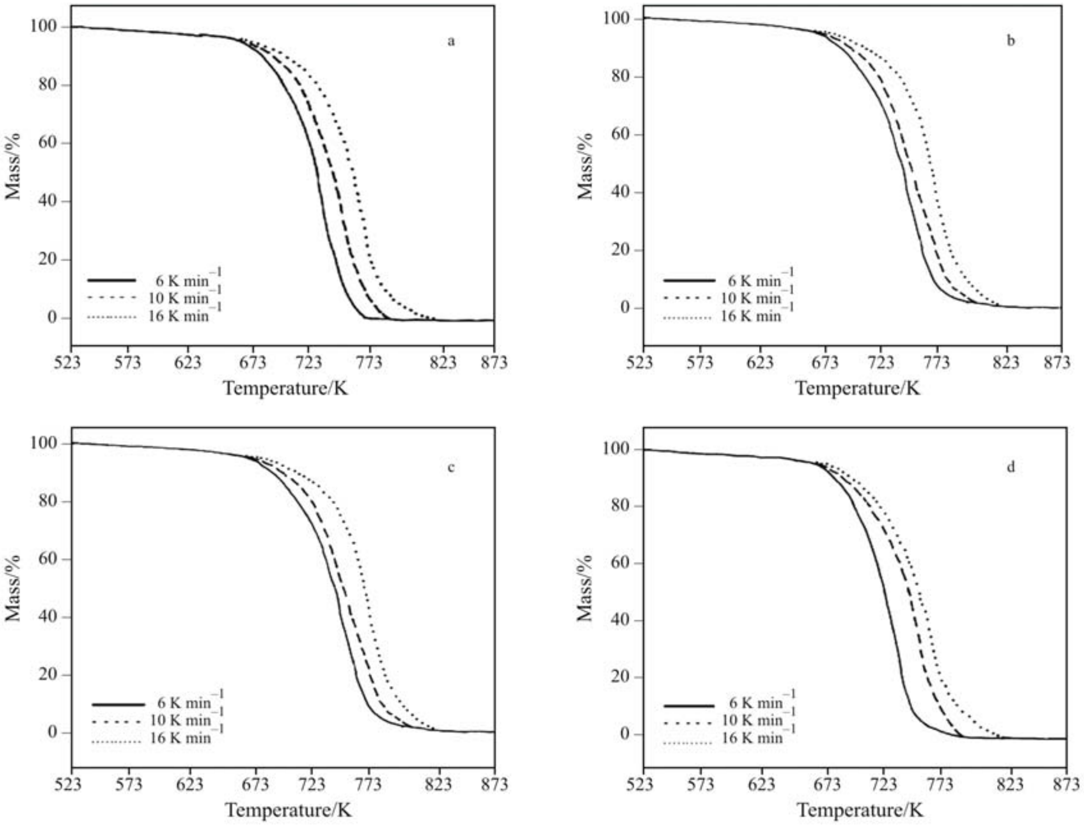

Fig. 1 TG curves of UHMWPE composites with different amounts of FMC (mass %) obtained at different heating rates: a – pure UHMWPE; b – 1.5; c – 3.0; d – 6.0 FMC%

Results and discussion

The TG curves of the pure UHMWPE and its composites with 1.5, 3.0 and 6.0 mass% FMC recorded in air at heating rates of 6, 10 and 16 K min^{-1} are presented in Fig. 1. It can be seen that the thermal decompositions of pure UHMWPE and its composites are one-step processes.

Obviously, the TG curves of UHMWPE and the composites based on it were shifted to higher temperatures with the increase of the heating rate. Besides, the heating rate affected significantly the temperature characteristics of the composites. Table 1 shows the main temperature characteristics of the composites obtained – initial temperature of degradation (T_d^i), temperatures at 10, 25 and 50 mass% mass loss (T_{10}, T_{25}) and (T_{50}), maximum rate of decomposition ($T_\mathrm{d}^\mathrm{max}$) and end temperature of decomposition (T_d^f). All these parameters were found to increase with the increase of the heating rate from 6 to 16 K min^{-1}.

The E_a and A [Eq. (10)] for each $g(\alpha)$ function can be calculated at constant heating rate from the fitting of $\ln\frac{g(\alpha)}{T^2}$ *vs*. $1/T$ plots. With properly selected expression of the $g(\alpha)$ function, straight lines with high values of the linear regression correlation coefficient R^2 can be obtained. The slope of the straight line gives the value of E_a and the cut off from the ordinate – the pre-exponential factor A. The highest correlation coefficient R^2 was obtained for D_3 (three dimentional diffusion described by the Jander equation) and A_1, F_1 (described by the Avrami–Erofeev equation for random nucleation and its subsequent growth) degradation mechanisms. The values of E_a, R^2 and $\ln A$ for these mechanisms calculated by the Coats–Redfern method are listed in Table 2.

The results obtained by the Coats–Redfern method showed that the most probable mechanism of thermal decomposition of pure UHMWPE in air at different heating rates was the D_3 mechanism (three-dimensional diffusion). For CM based on UHMWPE, the increase of FMC content and heating rate changed the mechanism of thermal degradation to a concurrence between D_3 and A_1,F_1 mechanisms. Here, the more probable mechanism at low content of FMC and higher heating rate was D_3 while A_1,F_1 was more probable at higher content of FMC and lower heating rates. At higher content of FMC and higher heating rate, random nucleation (A_1) is the more probable mechanism. This is because UHMWPE is molten under these conditions and its degradation is

Table 1 Temperature characteristics of UHMWPE composites containing different amounts of FMC

Heating rate/K min^{-1}	Content of FMC/mass%	T_d^i/K	T_{10}/K	T_{25}/K	T_{50}/K	T_d^{max}/K	T_d^f/K
6	0	653	668	703	723	728	765
	1.5	648	678	713	728	733	763
	3.0	663	678	713	728	758	763
	6.0	673	688	713	733	743	763
10	0	643	668	703	738	738	773
	1.5	663	678	718	743	743	783
	3.0	658	673	708	728	753	783
	6.0	673	683	718	743	743	783
16	0	638	678	733	753	763	813
	1.5	653	682	733	753	763	803
	3.0	653	683	733	753	758	803
	6.0	658	688	723	753	763	803

Table 2 Mechanism of degradation and kinetic parameters of UHMWPE composites containing different amounts of FMC calculated by Coats–Redfern method

Heating rate/K min^{-1}	Content of FMC/mass%	Mechanism of degradation					
		D_3 mechanism			A_1,F_1 mechanism		
		R^2	E_a/kJ mol^{-1}	ln A	R^2	E_a/kJ mol^{-1}	ln A
6	0	0.9964	360.5	56.2	–	–	–
	1.5	0.9808	405.0	63.5	0.9827	209.1	33.1
	3.0	0.9686	468.5	73.7	0.9749	247.5	39.4
	6.0	0.9693	511.2	71.4	0.9790	272.8	43.6
10	0	0.9785	343.3	53.1	–	–	–
	1.5	0.9967	361.1	55.3	0.9890	196.2	30.8
	3.0	0.9881	355.3	50.1	0.9898	196.5	27.7
	6.0	0.9847	402.9	62.2	0.9886	219.4	34.7
16	0	0.9888	289.9	43.6	–	–	–
	1.5	0.9884	346.6	53.3	0.9867	187.6	29.4
	3.0	0.9865	346.4	43.5	0.9806	188.3	22.8
	6.0	0.9836	351.9	53.3	0.9827	188.3	29.5

initiated at the interface between the liquid phase and the solid phase of FMC particles.

Table 2 shows also that the activation energy of degradation of the pure UHMWPE decreased with the increase of the heating rate and its values were between 289.6 and 360.5 kJ mol^{-1}. For based on UHMWPE with FMC and D_3 mechanism, A_1,F_1 also decreased with the increase of FMC content in the composites. Besides, E_a increased with FMC content in CM at the same heating rate 405.0–511.2, 361.1–402.9 and 346.6–351.9 kJ mol^{-1}, respectively. For the A_1,F_1 mechanism, the values of E_a were lower and their dependence on heating rate was weaker – E_a was from 187.6 to 272.8 kJ mol^{-1}. Similar values of the activation energy (333.2–343.2 kJ mol^{-1}) have been obtained by other authors [10] but for HDPE. The properties of HDPE are closer to these of UHMWPE than these of LDPE.

These observations lead to the conclusion that the degradation process of CM based on UHMWPE with FMC was controlled by both mechanisms discussed (which had the highest correlation coefficients of linear regression R_2), while for the pure UHMWPE the controlling mechanism was D_3.

The relationship between E_a and A of heterogeneous reactions is often described by a compensation equation [16]:

$$\ln A = \ln k_{iso} + \frac{E_a}{RT_{iso}} \qquad (11)$$

This equation implies the correlation of E_a, as a parameter influencing and indicating the system reactivity, with the parameters that compensate its influence (A and temperature interval in which the reactions take place).

The dependences of ln$A$ *vs.* E_a for UHMWPE/FMC composites calculated according to the D_3 and A_1,F_1 mechanisms, respectively, and for the pure UHMWPE according to the D_3 mechanism, are shown in Fig. 2.

Table 3 Values of the changes of entropy, enthalpy and Gibbs free energy of UHMWPE composites at different contents of FMC

Heating rate/K min^{-1}	Content of FMC/mass%	Mechanism of degradation					
		D$_3$ mechanism			A$_1$,F$_1$ mechanism		
		$\Delta H^{\#}$/kJ mol^{-1}	$\Delta S^{\#}$/J mol^{-1} K^{-1}	$\Delta G^{\#}$/kJ mol^{-1}	$\Delta H^{\#}$/kJ mol^{-1}	$\Delta S^{\#}$/J mol^{-1} K^{-1}	$\Delta G^{\#}$/kJ mol^{-1}
6	0	360.5	–286.8	564.6	–	–	–
	1.5	398.8	–284.0	609.8	202.9	–287.5	416.5
	3.0	462.3	–276.0	667.4	241.3	–292.5	458.7
	6.0	505.0	–294.4	723.8	266.7	–276.6	472.2
10	0	343.3	–294.0	558.4	–	–	–
	1.5	354.8	–294.4	579.4	189.9	–287.7	409.4
	3.0	349.1	–280.0	557.2	190.2	–294.5	412.1
	6.0	396.7	–294.7	618.6	213.2	–293.8	437.3
16	0	283.3	67.1	236.2	–	–	–
	1.5	340.2	148.0	227.3	181.2	–280.7	395.4
	3.0	340.1	66.5	289.3	182.0	–278.1	394.1
	6.0	345.6	148.4	232.4	181.9	–280.0	395.6

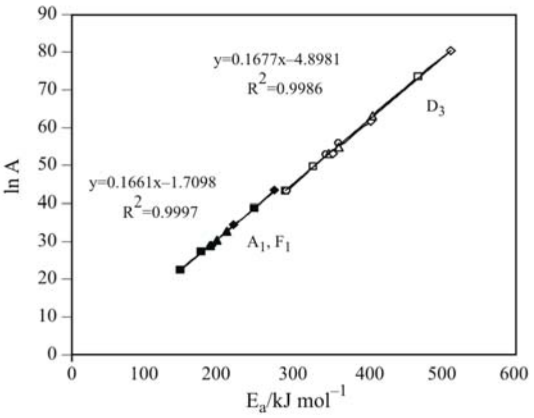

Fig. 2 Dependence of ln *A vs.* E_a of UHMWPE composites at different contents of FMC (mass%); mechanism D$_3$: ○ – pure UHMWPE; △ – 1.5; □ – 3.0; ◇– 6.0; mechanism A$_1$, F$_1$: ▲ – 1.5; ■ – 3.0; ◆ – 6.0 FMC%

It can be seen that two straight lines formed for both mechanisms D$_3$ and A$_1$,F$_1$ which confirmed the statement about the concurrency between the two mechanisms during the thermal degradation of CM based on UHMWPE and FMC.

According to the theory of the activated complex (transition state) of Eyring [14], the following equation can be written:

$$A = \frac{e\chi k_B T_p}{h} \exp\left(\frac{\Delta S^{\#}}{R}\right) \tag{12}$$

where e=2.7183 is the Neper number; χ – the transition factor, which is unity for monomolecular reactions; k_B – Boltzmann constant; h – Plank constant, and T_p - the peak temperature of DTA curve. Since

$$\Delta H^{\#} = E - RT_p \tag{13}$$

the changes of the enthalpy $\Delta H^{\#}$ and Gibbs free energy $\Delta G^{\#}$ for the activated complex formation from the reagent can be calculated using the well known thermodynamic equation:

$$\Delta G^{\#} = \Delta H^{\#} - T_p \Delta S^{\#} \tag{14}$$

The values of $\Delta S^{\#}$, $\Delta H^{\#}$ and $\Delta G^{\#}$ were calculated at T=T_P, since this temperature characterizes the highest rate of the process and, therefore, it is its important parameter.

The values of $\Delta S^{\#}$, $\Delta H^{\#}$ and $\Delta G^{\#}$ for UHMWPE and its composites with FMC calculated at the different rates used in the experiments are presented in Table 3.

It can be seen that $\Delta H^{\#}$ increased with the increase of FMC content for both degradation mechanisms. Besides, at lower heating rates, the active complex is characterized by a much higher 'degree of arrangement' which is determined by the negative values of $\Delta S^{\#}$ for the formation of the active complex [17]. At higher heating rates (16 K min^{-1}), the characteristic temperatures of thermal degradation (e.g. T_{50}, T_d^{max}) shifted to higher temperatures due to the overheating of the system. It is well known that the increase of the temperature of these systems results immediately in higher rates of the chemical reactions. Therefore, the positive values of $\Delta S^{\#}$ obtained at higher heating rates are probably resulting from the impossibility for arrangement of the activated complex in the transition state. The positive values of $\Delta G^{\#}$ showed that the process of thermal degradation of the composite materials studied was not spontaneous.

Conclusions

The mechanism of thermal decomposition of composite materials based on ultra-high molecular mass polyethene with fiber monocrystals was studied by the Coats-Redfern method in static air. It was found that two mechanisms are concurring during the degradation – diffusion D_3 and A_1F_1, while the initial polymer degraded only along the D_3 mechanism. The activation energy, change of entropy, enthalpy and Gibbs energy of these materials were calculated.

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