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STUDY ON THE KINETICS OF THERMAL DEGRADATION AFTER UV IRRADIATION OF POLYETHYLENE OXIDE FILMS CONTAINING COBALT (III) ACETYLACETONATE ADDITIVE

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Study on the Kinetics of Thermal Degradation after UV Irradiation of Polyethylene Oxide Films Containing Cobalt (III) Acetylacetonate Additive: *Polyethylene oxide films with cobalt (III) acetylacetonate additive were prepared and characterized after exposure to UV light, and compared with non-irradiated films of the precursor polyethylene oxide. The use of the studied additive caused double decrease of the sample strength after UV-irradiation for 1.5 and 5 hours, and reduction of the elongation at break from 970% to 30%, compared to the initial films. Thermogravimetric analyses was carried out under non-isothermal conditions in nitrogen atmosphere at constant heating rate. The Coats-Redfern method was used for calculation of the kinetic parameters of the thermal degradation of the films. Using the method of least squares linear regression the most probable mechanism function was determined. The lifetime of the composite films was significantly longer, which was a proof that the cobalt (III) acetylacetonate additive had enhanced thermal stability of the polyethylene oxide films.*

Key words*: non-isothermal TGA, polyethylene oxide films, cobalt (III) acetylacetonate, UV light, kinetic parameters*

INTRODUCTION

The values of the activation energy E_A under non-isothermal kinetics of degradation of polyethylene oxide (PEO) in the literature were in the range of 129 – 314 kJ/mol [1–5]. The most probable theoretical kinetic models describing the process were $F_{0.5}$, A_1, and $A_{1.5}$ with values of E_A of 129 kJ/mol [1], 274.5 [4] and 206 kJ/mol [5], respectively. According to Pielichowski and Flejtuch [3] the mathematical expression of the kinetic model f(α) of the non-isothermal degradation of PEO determined by non-regression analysis was R_3 with activation energy from 140 to 185 kJ/mol. However, these kinetic data of destruction of PEO films did not show the effect of the exposure to UV light, and were mainly related to the determination of the kinetic parameters with change of the molecular weight of the polymer. In our previous work the kinetic parameters at non-isothermal degradation of non-irradiated and irradiated with UV light PEO films were determined using Coats-Redfern method [6]. It was found that the exposure to UV light resulted in an increase of activation energy with about 60 kJ/mol, compared to the non-irradiated PEO foils, and the most probable mechanism function of thermal degradation was F_n, as the value of n was in the range of 0.34 to 0.88. The addition of 4 mmol/kg iron (III) acetylacetonate to foils of PEO and exposure to UV light did not affect the mechanism of thermal degradation, but the value of n for composition PEO films was in the range of 0.37 to 1.81 [7]. Moreover, the lifetime of pure PEO films irradiated with UV light for 5 hours was increased [6], while the lifetime of films containing organic complex of iron (III) acetylacetonate decreased [7].

The purpose of the present study was to be determined the effect of cobalt (III) acetylacetonate additive (Co(acac)$_3$) on the kinetics of non-isothermal degradation of polyethylene oxide films after their exposure to UV irradiation.

EXPERIMENTAL

Materials

To prepare the films were used powdery polyethylene oxide, product of Neochim Co., Dimitrovgrad, Bulgaria, melting temperature 68°C, molecular weight $M_V = 2.7\times10^6$ and cobalt (III) acetylacetonate, product of Merck, Germany, chemical formula $Co(C_5H_7O_2)_3$, melting temperature 210–213°C, molar weight 356.26 g/mol, density 1.43 g/cm^3.

Samples preparation

The initial PEO and the compositions, containing 4 mmol/kg Co(acac)$_3$, were homogenized in a laboratory mixer MPW-802 (Poland) at a rate of 10 s^{-1} for 15 min and then pressed in a laboratory press PHI (England) between aluminium foils under the following conditions: samples thickness about 200 μm, temperature 190°C, melting period 3 min at 190°C, pressing pressure 22 MPa for 1 min and cooling rate 40°C/min.

UV exposure

The samples formed as films with 200 μm thickness were exposed to UV light with wavelength in the interval 185–254 nm emitted by 5 lamps of 8 W each, at room temperature, for 1.5 or 5 hours.

Tensile testing

The tensile strength and elongation at break of the initial and composition PEO films, exposed to UV light, were measured on a dynamometer INSTRON 4203 (England) at room temperature and at speed of 50 mm/min.

Thermogravimetric measurements

The thermogravimetric analyses (TG-DTG-DSC) were carried out using a simultaneous thermal analyzer Netzsch STA 449 F3 Jupiter (Germany). Sample mass was about 4.2 ± 0.1 mg and the hearing rate was 12.243°C/min. The heating of the samples under non-isothermal conditions was conducted from room temperature to about 600°C, in a flow of nitrogen at a rate of 10 cm^3/min. The samples were loaded in an open platinum crucible without pressing and without using of a standard reference material.

RESULTS AND DISCUSSION

PEO films without additive and non-irradiated with UV light (PEO0), and such containing 4 mmol/kg Co(acac)$_3$ and irradiated with UV light for 1.5 hours (PEO1.5+4Co) and for 5 hours (PEO5+4Co) were studied. Strength and elongation at break are very important properties of the polymer materials, because they correspond to their possibility for destruction. Moreover, the process of destruction always is related to deterioration of the mechanical properties. The decrease of the values of these parameters can be related to the decrease of the polymer molecular weight and formation of defects on the sample surface inflicted by the UV irradiation. For this reason, the dependencies of the tensile strength and the elongation at break of the composite films on the irradiation duration with UV light were studied. It was found that the tensile strength of the samples of PEO films containing 4 mmol/kg Co(acac)$_3$ after UV exposure for 1.5 hours decreased 2 times, compared with that of the initial PEO films. The reduction of this parameter was the same for the samples irradiated for 5 hours. It was observed a sharp reduction of the elongation at break from 970% for non-irradiated PEO foils to 30% for the foils with additive exposed to UV irradiation for 1.5 and 5 hours.

The temperatures of melting and crystallization of the samples PEO1.5+4Co and PEO5+4Co remained unchanged and were ~ 67°C and 146°C, respectively. The degree of crystallinity of the samples was calculated at $\Delta H_{100\%} = 197$ J/g for 100% crystalline PEO [8]. The irradiation with UV light caused increase in the degree of crystallinity from 70% for the non-irradiated initial PEO films to 80% for the irradiated materials containing cobalt (III) acetylacetonate. A similar increase of the degree of crystallinity as a result of the UV exposure was reported for PEO films containing iron (III) acetylacetonate additive [7].

Based on the thermogravimetric data, it was observed that the thermal degradation of the studied PEO films (PEO0, PEO1.5+4Co and PEO5+4Co) was a single-step process (Fig. 1A). The initial and the final temperature of thermal degradation was determined from the TG curves (Table 1). It can be seen that the initial temperature shifted towards higher temperature for the composition polymer films exposed to UV light, and the shift was with around 17 and 30°C. The final temperature shifted towards higher temperature also, but this shift was only with about 1 and 3°C. The peak temperature T_{peak} of each sample was determined from the DTG curves (Fig. 1B). The value of T_{peak} for PEO0 was 400.1°C, which was almost the same as that reported by Pielichowski and Flejtuch [3]. The shift for the irradiated composite films (PEO1.5+4Co and PEO5+4Co) was insignificant, with about 1–2°C. The process of thermal degradation was accompanied by an endothermic effect (Fig. 1C). The peak temperatures determined from the DSC curves are given in Table 1.

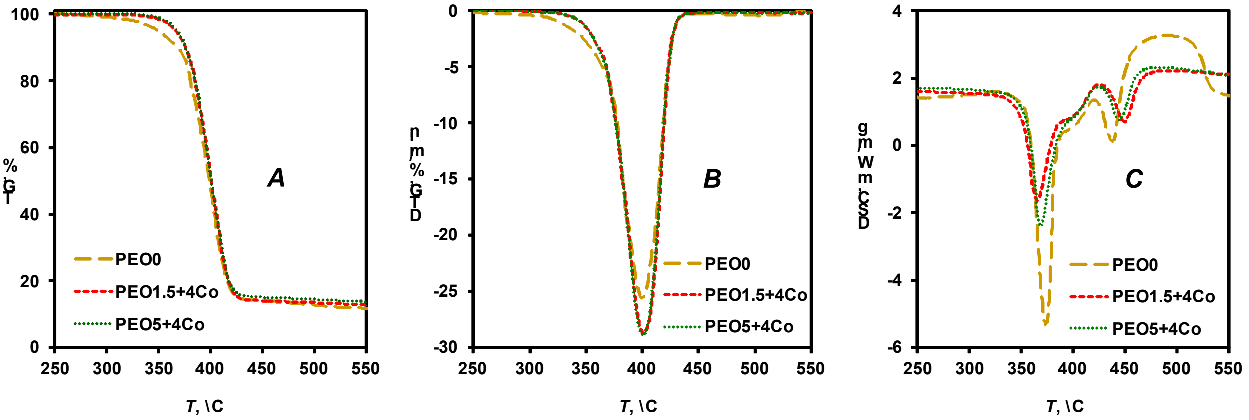

Fig. 1. TG (*A*), DTG (*B*) and DSC (*C*) curves at a heating rate of 12.243°C/min for non-irradiated initial PEO films (PEO0) and PEO films containing 4 mmol/kg Co(acac)$_3$ exposed to UV light for 1.5 h (PEO1.5+4Co) and 5 h (PEO5+4Co).

Table 1. Characteristic temperatures of the TG, DTG, and DSC curves obtained by the thermal degradation of PEO films: pure non-irradiated (PEO0) and such ones containing 4 mmol/kg Co(acac)$_3$, exposed to UV light for 1.5 (PEO1.5+4Co) and 5 hours (PEO5+4Co).

Sample	T_{initial}, °C	T_{peak}, °C	T_{final}, °C	$T_{\mathrm{peak(I)}}$, °C	$T_{\mathrm{peak(II)}}$, °C
PEO0	259.7	400.1	490.8	374.0	438.5
PEO1.5+4Co	287.0	401.7	492.0	366.2	449.8
PEO5+4Co	290.2	401.1	484.2	369.8	445.1

The kinetic parameters of the thermal degradation of the studied films were determined by non-isothermal thermogravimetric analysis. The mathematical apparatus, which was used in the present work, was described in details earlier [6,7]. In Table 1 are summarized the basic equations used herein, where α is the conversation degree; m_{i}, m_t and m_{f} are the initial, current and final sample mass; t is the time; dα/dt is the kinetic model of thermal degradation; T is the absolute temperature; k(T) is the dependence of the rate constant on the temperature; f(α) is a function which type depends on the reaction mechanism; A is the pre-exponential factor in the Arrhenius equation; E_{A} is the activation energy; R is the universal gas constant equal to 8.314 J/(mol.K); q = dT/dt is the heating rate which must be constant; g(α) is the integral form of the f(α) function and depends on the conversion mechanism and its mathematical model; e is the Napier number equal to 2.7183; χ is the transmission coefficient which is unity for monomolecular reactions; k_{B} is the Boltzmann constant; h is the Planck constant; T_{peak} is the peak temperature on the DTG curve; $\Delta S^{\neq}$ is the change of the entropy, $\Delta H^{\neq}$ is the change of the enthalpy, and $\Delta G^{\neq}$ is the change of Gibbs free energy for the formation of the activated complex from the reactants; t_f is the lifetime and n is the reaction order.

The algebraic expressions f(α) and g(α) functions of the most common reaction mechanisms of thermal decompositions for solid state reactions depending on the kinetic model are given in the literature [9]. Using the method of Coats-Redfern [10], the right-hand side of Eq. (6) was solved on the basis of the TG curves at a single heating rate equal to 12.243°C/min. The values of the activation energy, the pre-exponential factor and the most probable mechanism of the reactions were determined by the linear form of the Coats-Redfern equation (Eq. (7) in Table 2) from the data of the TG curves in the range of conversion degree α of 0.05 to 0.95. The dependence of ln[g(α)/T^2] versus 1/T was plotted (not shown) using the mathematical expressions of each g(α) function. The coefficient of determination R^2 was used as a criterion for selection of the most probable mechanism function. In Table 3 are given three g(α) functions with their values of R^2 which have to be as close as possible to unity, and the corresponding values of the activation energy E_A.

Table 2. Mathematical apparatus.

Mathematical expression	Equation
$\alpha = \frac{m_\mathrm{i} - m_\mathrm{t}}{m_\mathrm{i} - m_\mathrm{f}}$	(1)
$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = \mathrm{k}(T)\mathrm{f}(\alpha)$	(2)
$k = A\exp\left(-\frac{E_\mathrm{A}}{RT}\right)$	(3)
$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = A\exp\left(-\frac{E_\mathrm{A}}{RT}\right)\mathrm{f}(\alpha)$	(4)
$\int_0^\alpha \frac{\mathrm{d}\alpha}{\mathrm{f}(\alpha)} = \frac{A}{q}\int_0^T \exp\left(-\frac{E_\mathrm{A}}{RT}\right)\mathrm{d}T$	(5)
$g(\alpha) = \frac{A}{q}\int_0^T \exp\left(-\frac{E_\mathrm{A}}{RT}\right)\mathrm{d}T$	(6)
$\ln\frac{\mathrm{g}(\alpha)}{T^2} = \ln\frac{AR}{qE_\mathrm{A}} - \frac{E_\mathrm{A}}{RT}$	(7)
$A = \frac{e\chi k_\mathrm{B}T_\mathrm{peak}}{h}\exp\left(\frac{\Delta S^{\neq}}{R}\right)$	(8)
$\Delta H^{\neq} = E_\mathrm{A} - RT_\mathrm{peak}$	(9)
$\Delta G^{\neq} = \Delta H^{\neq} - T_\mathrm{peak}\Delta S^{\neq}$	(10)
$t_\mathrm{f} = \frac{\left(1-0.95^{1-n}\right)}{A(1-n)}\exp\left(\frac{E_\mathrm{A}}{RT}\right)$	(11)

Table 3 Three of the best fitting kinetic models (types of g(α) functions) and calculated values of the activation energy E_A of PEO films: pure and such ones containing 4 mmol/kg Co(acac)$_3$, irradiated with UV light for 1.5 and 5 hours.

№	PEO0			PEO1.5+4Co			PEO5+4Co		
	Mechanism	E_A, kJ/mol	R^2	Mechanism	E_A, kJ/mol	R^2	Mechanism	E_A, kJ/mol	R^2
1	D_2	337.71	0.9905	$F_{n = 1.1541}$	276.81	1.0000	$F_{n = 1.2000}$	285.80	1.0000
2	D_4	348.26	0.9905	A_1, F_1	263.31	0.9994	D_5	607.31	0.9996
3	$F_{n = 0.3405}$	164.45	0.9901	$A_{1/3}$	171.86	0.9994	A_1, F_1	268.33	0.9990

As can be seen in Table 3 the difference between the determination coefficients for samples PEO0 was insignificant, but the calculated values of E_A for D_2 and D_4 mechanism functions did not correspond to diffusion mechanism as they were too high. The value of E_A was used as another criterion in the selection of the best $g(\alpha)$ functions. The F_n function was chosen as the most probable mechanism function for all the samples. Using the Excel solver tool the value of the reaction order n for each sample was calculated. The calculated values of n, E_A and A are given in Table 4. The value of E_A for PEO0 (164.45 kJ/mol) was within the range 140–185 kJ/mol given in the reference [3]. The reaction order for the PEO0 films was about 1/3. The reaction order for the PEO films containing Co(acac)$_3$ was about 1.2. Comparing the effect of duration of exposure of the composite films it was found that longer irradiation resulted in a very slight increase in the value of n.

Table 4 Values of the reaction order n, activation energy E_A, pre-exponential factor A in the Arrhenius equation, change of enthalpy $\Delta H^{\neq}$, change of entropy $\Delta S^{\neq}$, and change of Gibbs free energy $\Delta G^{\neq}$ for PEO films: pure and such ones containing 4 mmol/kg Co(acac)$_3$, exposed to UV light for 1.5 and 5 hours.

Sample	n	E_A, kJ/mol	A, 1/min	R^2	ΔS, J/(mol.K)	ΔH, kJ/mol	ΔG, kJ/mol
PEO0	0.3405	164.45	1.27×10^{12}	0.9901	–62.34	158.85	200.82
PEO1.5+4Co	1.1541	276.81	4.15×10^{20}	1.0000	100.65	271.19	203.27
PEO5+4Co	1.2000	285.80	2.51×10^{21}	1.0000	115.62	280.20	202.24

It was found previously [6] that the activation energy of irradiated PEO films no containing additive was higher than that of non-irradiated ones which was fully in line with the findings of Doytcheva *et al.* [11] that PEO was crosslinked by exposure to ultraviolet radiation. The addition of 4 mmol/kg Co(acac)$_3$ and the UV irradiation resulted in increased stability of the PEO films since the value of E_A was higher by more than a hundred kJ/mol for samples PEO1.5+4Co and PEO5+4Co. Doytcheva *et al.* [11] have found that photochemical crosslinking of PEO proceeds in the presence of photoinitiators which act as a hydrogen-abstracting agent. The same effect was found herein for the Co(acac)$_3$ additive. The values of the pre-exponential factor A for solid state reactions usually vary with six or seven orders of magnitude. As can be seen in Table 4 the exposure to UV light of the PEO films containing 4 mmol Co(acac)$_3$ per kg PEO resulted in the increase of this kinetic parameter which had 8–9 orders of magnitude higher value. The high factor usually indicates "loose" complex [9].

The values of $\Delta S^{\neq}$, $\Delta H^{\neq}$ and $\Delta G^{\neq}$ for the formation of the activated complex from the reactants were calculated at T_{peak}. The value of $\Delta S^{\neq}$ for PEO0 was negative, i.e. the activated complex was more "organized" than the initial reactants. For the samples with Co(acac)$_3$ additive the values of $\Delta S^{\neq}$ were positive, which meant that the activated complex was with lower degree of arrangement than the initial reagents, corresponding to the higher number of degrees of freedom in the Gibbs' phase rule. The values of $\Delta H^{\neq}$ were positive for all samples, showing that the process of their thermal degradation was connected with the introduction of heat. Moreover, the need of heat introduction for thermal destruction of PEO1.5+4Co and PEO1.5+4Co films was higher by about 120 kJ/mol than that of PEO0 films. The values of $\Delta G^{\neq}$ were also positive, with a value of about 202 kJ/mol, indicating that the decomposition of the films was not spontaneous process.

The lifetime t_f is defined as the time when the mass loss reaches 5 mass%., and it is very useful in the selection of polymers. If the reaction mechanism is F_n and $n \neq 1$, then t_f can be calculated on the basis of data from the thermal analysis using Eq. (11). t_f was calculated in the temperature range 25–200°C and the plotted curves are shown in Fig. 2.

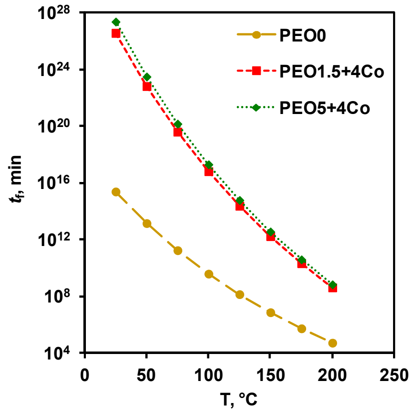

Fig. 2 Dependence of the lifetime t_f on the temperature for non-irradiated initial PEO films (PEO0) and PEO films containing 4 mmol/kg Co(acac)$_3$ exposed to UV light for 1.5 h (PEO1.5+4Co) and 5 h (PEO5+4Co).

In Fig. 2 can be seen that the lifetime steeper decreased with the increase in the temperature. For the PEO1.5+4Co and PEO1.5+4Co films t_f was higher than that of PEO0 films. The results showed that if it is desired to be prepared PEO films with long-term use they must be composite materials containing an appropriate additive, such as Co(acac)$_3$, and irradiated with UV light, if the studied additive is used – for 1.5–5 hours.

CONCLUSIONS

For polyethylene oxide films containing 4 mmol/kg cobalt (III) acetylacetonate and irradiated with UV light for 1.5 or 5 hours the obtained results and calculations showed that the tensile strength decreased two times and the elongation at break reduced to 30%, compared with that of the non-irradiated pure polyethylene oxide films. It was determined that the mechanism of thermal degradation was F_n and the process of destruction was not spontaneous and need heat introduction in all cases. Moreover, polyethylene oxide films with long-term use can be prepared using the additive studied in quantity 4 mmol/kg polymer, as they must be irradiated with UV light for about 1.5–5 hours.

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