

**ВЛИЯНИЕ НА ДОБАВКАТА ОТ ЖЕЛЕЗЕН (III) АЦЕТИЛАЦЕТОНАТ И
ЕКСПОЗИЦИЯТА НА УВ-СВЕТЛИНА ВЪРХУ ТЕРМИЧНИТЕ И ЯКОСТНИТЕ
ХАРАКТЕРИСТИКИ НА ФИЛМИ ОТ ПОЛИЕТИЛЕН ОКСИД**

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**EFFECT OF IRON (III) ACETYLACETONATE ADDITIVE AND UV EXPOSURE ON
THE THERMAL AND TENSILE CHARACTERISTICS OF POLYETHYLENE OXIDE
FILMS**

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ABSTRACT

Polyethylene oxide films with iron (III) acetylacetonate additive were obtained and characterized after exposure to UV light. The analysis of the tensile properties of the materials containing additive upon irradiation for 5 hours showed that the tensile strength and elongation at break sharply decreased. To determine the kinetic parameters and the most probable mechanism of the thermal degradation of the studied films under non-isothermal conditions in an inert atmosphere at constant heating rate the Coats-Redfern method was used. It was found that the addition of 4 mmol/kg iron (III) acetylacetonate to the polymer and the exposure for 5 hours to the action of UV light caused a change in the kinetic equation order of the most probable mechanism function of the reaction. The values of the activation energy, change of entropy, enthalpy and Gibbs free energy for the formation of the activated complex from the reactants were calculated for the studied polymer materials.

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

INTRODUCTION

Polyethylene oxide (PEO) is a polymer which upon exposure to UV light in the presence of oxygen is susceptible to oxidative degradation. This is due to the formation of reactive intermediates such as hydroperoxides and free radicals. Destruction as a result of the oxidation leads to modification of the chemical structure of PEO, change of the molecular weight, crystallinity and mechanical properties.

The destruction process of polymers initiated by the action of UV light in the presence of oxygen is called oxidative photodegradation or photooxidation. Although the polyethylene oxide does not absorb radiation at a wavelength above 200 nm, it may contain structural defects or impurities that act as photoinitiators. Thus the absorbed energy can be transferred to the "weaker" bonds and they break. The main effects on polymers of exposure to UV light are: scission of the main polymer chain, breaking away of side groups or introduction of new functional groups, and can also occur processes of cross-linking [1]. As a rule, methods to impart ability of polymers to degrade under the influence of light are the use of special additives or the introduction of light-sensitive groups in their compositions. The blending of polymer materials with pro-oxidants in the form of complexes of transition metals under accelerated conditions of exposure is an effective way to increase their degree of oxidation.

Although the destruction of PEO under irradiation with UV light has been widely reported in the literature the study and analysis of these materials is complicated by the fact that the precise mechanisms of the processes occurring in the photooxidation are not fully established [2, 3]. A number of authors have found that in the presence of small amounts of inorganic salts of transition metal ions (FeCl₃, CuCl₂, NiCl₂ and CoCl₂) upon exposure to UV light in the presence of oxygen strongly reduced the photostability of PEO [4–7]. The authors have not found in the literature any research articles on the use of additives of organic complexes of polyvalent metals in PEO.

Therefore, the purpose of this work was to study the tensile and thermal properties of polyethylene oxide films containing iron (III) acetylacetonate additive, exposed to UV light for different times.

EXPERIMENTAL

Materials

For the preparation of the films were used powdery polyethylene oxide (PEO), product of Neochim Co., Dimitrovgrad, Bulgaria, with melting temperature 68°C and molecular weight $M_v = 2.7 \times 10^6$ and iron (III) acetylacetonate $\text{Fe}(\text{acac})_3$ with chemical formula $\text{Fe}(\text{C}_5\text{H}_7\text{O}_2)_3$, melting temperature 180–182°C, molar weight 353.17 g/mol and density 5.24 g/cm³, product of Merck, Germany.

Samples preparation

The initial PEO and the compositions containing 4 mmol/kg $\text{Fe}(\text{acac})_3$ 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. The conditions of films preparation were as follows: 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 200 µm thick films were irradiated by UV light with wavelengths 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 PEO films and the PEO films containing 4 mmol/kg iron (III) acetylacetonate and 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). Samples of about 4.6 ± 0.1 mg mass were used for the experiments at a heating rate of 12°C/min up to 600°C in a flow of nitrogen at a rate of 10 cm³/min under non-isothermal conditions. The samples were loaded without pressing in an open (6 mm diameter and 3 mm height) platinum crucible, without using of a standard reference material. The degree of crystallinity of the samples was calculated at $\Delta H_{100\%} = 197$ J/g for 100% crystalline PEO [8].

RESULTS AND DISCUSSION

The tensile strength of the pure PEO films and of these with iron (III) acetylacetonate additive in an amount of 4 mmol/kg polymer was compared. It was found that the UV exposure for 5 hours had no significant effect on the strength of the initial PEO films. The tensile strength was in the range of 8.4 to 7.8 MPa for non-irradiated and irradiated for 5 hours PEO films, respectively, while the use of $\text{Fe}(\text{acac})_3$ at the same time of exposure to UV light reduced the tensile strength of the materials to 0.9 MPa. Such dependence for the elongation at break of the studied samples was obtained. Upon exposure time of 5 hours the elongation at break decreased from 970% to 650% for the containing no additive irradiated materials and to 10% for these with 4 mmol/kg iron (III) acetylacetonate, respectively.

For the resulting films of PEO, with and without additive, under the above-mentioned exposure times the temperatures of melting and crystallization, and the degree of crystallinity were determined. The irradiation with UV light of the foils of pure PEO and those containing $\text{Fe}(\text{acac})_3$ under accelerated conditions for 1.5 and 5 hours decreases the melting temperature (67.8–66.1°C) and increases the degree of crystallinity. The increase in the degree of crystallinity was most noticeable for the materials with iron (III) acetylacetonate – up to 93–94% as compared to the crystallinity degree of the non-irradiated initial PEO films which was ~ 70%. Probably, after

exposure to UV light, the short decomposed chains of the PEO surface reorganized, and thereby the crystallinity degree increased. The temperature of crystallization of all tested samples of PEO with and without additive of $\text{Fe}(\text{acac})_3$ before and after irradiation for 1.5 and 5 hours remained within the range 143.3–145.1°C.

Based on the data from the thermogravimetric analysis (Fig. 1) the thermal degradation of the PEO films non-containing additive and non-irradiated with UV light (PEO0), and these containing 4 mmol/kg $\text{Fe}(\text{acac})_3$ and irradiated with UV light for 1.5 hours (PEO1.5+4Fe) and 5 hours (PEO5+4Fe), respectively, was observed to be a single-step process, in all cases (Fig. 1A).

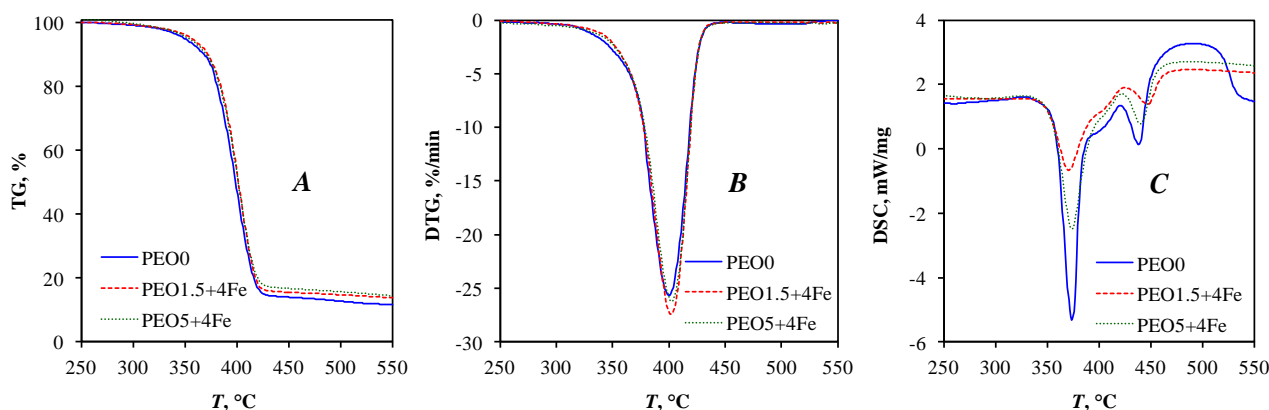


Fig. 1. TG (A), DTG (B) and DSC (C) curves at a heating rate of 12.244°C/min for non-irradiated PEO films (PEO0) and PEO films containing 4 mmol/kg $\text{Fe}(\text{acac})_3$ exposed to UV light for 1.5 h (PEO1.5+4Fe) and 5 h (PEO5+4Fe).

From the TG curves the initial and final temperature of thermal degradation was determined, which are given in Table 1. As can be seen therein, the initial temperature shifted towards higher temperature with the increase of irradiation times, and this shift was significant, while the final temperature shifted towards lower temperature, and this shift was only with about 6°C. On the basis of the DTG curves (Fig. 1B) the peak temperature T_{peak} of each sample was determined. The T_{peak} value of the non-irradiated films from pure PEO was 400.1°C, almost the same as that reported by other authors [9]. The shift of this temperature with the exposure to UV light was about 2.5°C. The decomposition process was accompanied by an endothermic effect (see Fig. 1C). The corresponding peak temperatures determined from the DSC curves are given in Table 1.

Table 1. Characteristic temperatures of TG, DTG, and DSC curves obtained by the thermal degradation of PEO films: pure and such ones containing 4 mmol/kg $\text{Fe}(\text{acac})_3$, irradiated with UV light for 1.5 and 5 hours.

Sample	T_{initial} , °C	T_{peak} , °C	T_{final} , °C	$T_{\text{peak(I)}}$, °C	$T_{\text{peak(II)}}$, °C
PEO0	259.7	400.1	490.8	374.0	438.5
PEO1.5+4Fe	266.4	402.6	488.4	371.0	447.1
PEO5+4Fe	292.2	402.5	485.2	373.8	441.2

The thermal degradation kinetic parameters of the films were determined by non-isothermal thermogravimetric analysis, where the reaction rate is expressed by the conversion degree α :

$$\alpha = \frac{m_i - m_t}{m_i - m_f}, \quad (1)$$

where m_i , m_f and m_t are the initial, final and current sample mass at moment t . The kinetic model of thermal degradation is given by the formula:

$$\frac{d\alpha}{dt} = k(T)f(\alpha), \quad (2)$$

where T is the absolute temperature; t is the time, and $f(\alpha)$ is a function which type depends on the reaction mechanism and $k(T)$ is the dependence of the rate constant on the temperature. The latter is almost universally represented by the Arrhenius equation:

$$k = A \exp\left(-\frac{E_A}{RT}\right), \quad (3)$$

where A is the pre-exponential factor, R is the universal gas constant equal to 8.314 J/(mol.K) and E_A is the activation energy.

Substituting Eq. (3) in (2) the following fundamental equation is obtained:

$$\frac{d\alpha}{dt} = A \exp\left(-\frac{E_A}{RT}\right) f(\alpha) \quad (4)$$

After some mathematical transformations at constant heating rate, i.e. $dT/dt = q = \text{constant}$, the following equation is written:

$$\int_0^\alpha \frac{d\alpha}{f(\alpha)} = \frac{A}{q} \int_0^T \exp\left(-\frac{E_A}{RT}\right) dT \quad (5)$$

The left-hand side of the Eq. (5) is denoted as $g(\alpha)$:

$$g(\alpha) = \frac{A}{q} \int_0^T \exp\left(-\frac{E_A}{RT}\right) dT \quad (6)$$

The algebraic expressions in differential form – $f(\alpha)$ functions, and in integral form – $g(\alpha)$ functions, of the most common reaction mechanisms of thermal decompositions for solid state reactions depending on the kinetic model are given in reference [10]. The right-hand side of Eq. (6) is solved on the basis of the TG curves at a single heating rate (equal to 12.244°C/min) by the method of Coats-Redfern [11]. 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 Coats-Redfern equation [11]:

$$\ln \frac{g(\alpha)}{T^2} = \ln \frac{AR}{qE_A} - \frac{E_A}{RT}, \quad (7)$$

To be determined the kinetic parameters E_A , A , the data of the TG curves in the range of conversion degree α of 0.05 to 0.95 were used. The dependence of $\ln[g(\alpha)/T^2]$ versus $1/T$ was plotted (not shown) using the mathematical expressions of each $g(\alpha)$ function [10]. The plot which gave a straight line was sought as the coefficient of determination R^2 was used as a criterion in selecting the most probable mechanism function. R^2 have to be as close as possible to unity. In Table 2 are given the three $g(\alpha)$ functions with the highest values of R^2 in decreasing order and the corresponding values of the activation energy E_A .

Table 2. The three best fitting kinetic models (types of $g(\alpha)$ functions) and calculated values of the activation energy E_A of PEO films: pure and such ones containing 4 mmol/kg Fe(acac)₃, irradiated with UV light for 1.5 and 5 hours.

№	PEO0			PEO1.5+4Fe			PEO5+4Fe		
	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	D ₄	385.94	0.9961	F _n	77.42	0.9788
2	D ₄	348.26	0.9905	D ₂	374.31	0.9961	F ₂	83.58	0.9779
3	F _n	164.45	0.9901	F _n	184.43	0.9960	D ₅	137.00	0.9757

As can be seen in Table 2 the difference between the determination coefficients for samples PEO0 and PEO1.5+4Fe was insignificant. If it was assumed that the degradation mechanism was of D₂ or D₄ instead of F_n, the calculated value of E_A would be inexplicably high. Therefore, the value of E_A was used as another criterion in the selection of the mechanism function. The F_n function was chosen as the most probable mechanism function for all of the PEO films. The value of the reaction order *n* for each sample was calculated using the Excel solver tool. They are presented in Table 3 together with the values of the activation energy E_A and the pre-exponential factor *A* in the Arrhenius equation.

Table 3. Values of the reaction order *n*, activation energy E_A, pre-exponential factor *A* in the Arrhenius equation, change of enthalpy ΔH[‡], change of entropy ΔS[‡], and change of Gibbs free energy ΔG[‡] for PEO films: pure and such ones containing 4 mmol/kg Fe(acac)₃, irradiated with UV light for 1.5 and 5 hours.

Sample	<i>n</i>	E _A , kJ/mol	<i>A</i> , 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+4Fe	0.3741	184.43	4.46×10 ¹³	0.9960	-32.76	178.81	200.95
PEO5+4Fe	1.8119	77.42	3.48×10 ⁵	0.9788	-187.99	71.80	198.82

As can be seen in Table 3 the reaction order increased from sample PEO0 to sample PEO5+4Fe. The obtained value of E_A for PEO0 (164.45 kJ/mol) was within the range 140–185 kJ/mol given in reference [1]. The reaction order *n* for the PEO1.5+4Fe film was a little bit higher as well as the value of the activation energy. The exposure to UV light for 5 hours led to a notable change in the reaction order for the film containing Fe(acac)₃ in a amount of 4 mmol/kg PEO. The reaction order *n* for the PEO0 film was around 1/3 while for the PEO5+4Fe it was around 2, which correspond to a chemical process or mechanism of thermal degradation non-involving equations.

In a previous study [12] it was found that the activation energy of irradiated films of PEO no containing additive was higher than that of PEO0. It has been assumed that cross-linking of the polymer upon UV irradiation lead to enhanced thermal stability of those films. However, the addition of Fe(acac)₃ result in increased degradability of the PEO films. When the exposure time was 1.5 hours the additive effect and the effect of UV light were competing with each other, while when the exposure time was 5 hours the pro-oxidant effect was prevailing. Besides, this preponderance also affected the value of the activation energy, as can be seen in Table 3, which was more than two times lower than that of PEO0.

The values of the pre-exponential factor *A* for solid state reactions usually vary with six or seven orders of magnitude. For first-order reactions the pre-exponential factor may vary in the range 10⁵–10¹⁶ 1/min. If the reaction is not dependent on surface area low factor may indicate “tight” complex, while high factor – “loose” complex [10]. As can be seen in Table 3 the exposure to UV light of the PEO films containing 4 mmol Fe(acac)₃ per kg PEO resulted in the insignificant increase of this kinetic parameter upon exposure for 1.5 hours, but upon exposure for 5 hours the pre-exponential factor had seven orders of magnitude lower value.

From the theory of Eyring [13] for the transition state, so-called activated complex, for the pre-exponential factor *A* in the Arrhenius equation can be written:

$$A = \frac{e \chi k_B T_{\text{peak}}}{h} \exp\left(\frac{\Delta S^\ddagger}{R}\right), \quad (8)$$

where *e* = 2.7183 is the Napier number, *χ* is the transmission coefficient which is unity for monomolecular reactions, *k_B* is the Boltzmann constant, *h* is the Planck constant, and *T_{peak}* is the peak temperature on the DTG curve.

The change of the enthalpy ΔH^\ddagger and the change of Gibbs free energy ΔG^\ddagger for the formation of the activated complex can be calculated using the following thermodynamic equations:

$$\Delta H^\ddagger = E_A - RT_{\text{peak}}, \quad (9)$$

$$\Delta G^\ddagger = \Delta H^\ddagger - T_{\text{peak}} \Delta S^\ddagger \quad (10)$$

The values of ΔS^\ddagger , ΔH^\ddagger and ΔG^\ddagger for the formation of the activated complex by the thermal degradation of the PEO films were calculated at T_{peak} , and they are presented in Table 3. It can be seen that the values of ΔG^\ddagger were positive (~ 200.2 kJ/mol), indicating that the process of degradation of the materials was not spontaneous. The values of ΔH^\ddagger were also positive, i.e. the thermal degradation process was connected with the introduction of heat. The trend of the values of ΔH^\ddagger was the same as that of the values of E_A . The need of heat introduction for thermal destruction of PEO5+4Fe film was lower by 87 kJ/mol than that of PEO0 film. For the formation of the activated complex the values of ΔS^\ddagger were negative, i.e. the activated complex formed were more structured or “organized” than the initial reactants. Because for the PEO1.5+4Fe film the value of ΔS^\ddagger being negative was higher than that of PEO0, and closer to zero, and the value of ΔS^\ddagger for PEO5+4Fe was much more negative, it could be assumed that at the thermal degradation of polyethylene oxide films containing $\text{Fe}(\text{acac})_3$ in a nitrogen atmosphere two competing processes occurred, namely destruction and recombination.

The parameter lifetime t_f is very useful in the selection of polymers especially when long- or short-term use is essential at their application. The lifetime can be determined on the basis of data from the thermal analysis or under conditions of accelerated ageing. This parameter is defined as the time when the mass loss reaches 5 mass%. If the reaction mechanism is F_n and $n \neq 1$, then t_f can be calculated by the following definitional equation [10]:

$$t_f = \frac{(1 - 0.95^{1-n})}{A(1-n)} \exp\left(\frac{E_A}{RT}\right), \quad (11)$$

where n is the reaction order.

The time required for degradation of 5 mass% of the studied PEO films in the temperature range 25–200°C was calculated using Eq. (11), and the plotted curves of the lifetime dependence on the temperature are shown in Fig. 2.

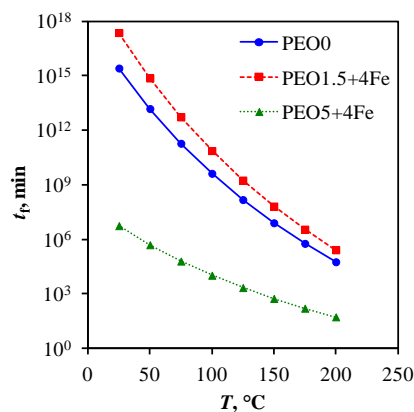


Fig. 2. Dependence of the lifetime t_f on the temperature for non-irradiated PEO films (PEO0) and PEO films containing 4 mmol/kg $\text{Fe}(\text{acac})_3$ exposed to UV light for 1.5 h (PEO1.5+4Fe) and 5 h (PEO5+4Fe).

It can be seen in Fig. 2 that the lifetime in nitrogen atmosphere of the PEO films steeper decreased with the increase in the temperature. For the PEO1.5+4Fe films t_f was higher, but for the PEO5+4Fe films was significantly lower. For films of PEO with long-term use it is necessary 1.5

hours UV exposure time, while for films with short-term use it is required 5 hours time of irradiation.

CONCLUSIONS

UV irradiated films on the basis of polyethylene oxide and 4 mmol/kg iron (III) acetylacetonate were prepared. The results obtained showed that the tensile strength and the elongation at break of irradiated for 5 hours polyethylene oxide films with additive decreased to 0.9 MPa and 10%, respectively. The mechanism of thermal degradation was defined as F_n mechanism, wherein n was approximately 0.3 for PEO0 and 2 for PEO5+4Fe films. The calculated positive values of ΔG^\ddagger of about 200 kJ/mol and ΔH^\ddagger mean that the process of destruction of PEO5+4Fe films was not spontaneous and it was necessary to introduce heat by 87 kJ/mol less. Because of the low values of the activation energy and pre-exponential factor the determined lifetime for the films with iron (III) acetylacetonate after 5 hours irradiation was lower.

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