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Effect of Metal Acetylacetonates on the Photooxidative Destruction of High Density Polyethylene

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The process of photooxidative destruction of high density polyethylene films containing different organic complexes of polyvalent metals as pro-oxidant additives after UV- irradiation was studied. During exposure to UV- irradiation, the more significant changes in the mechanical and thermal properties were detected for the foils containing pro-oxidant additives compared to initial high density polyethylene. This indicated for the higher degree of oxidation in these samples and confirmed the effectiveness of these additives in promoting the oxidation of high density polyethylene during UV-irradiation. It was found that the decrease of the strength of the initial high density polyethylene foils was more pronounced for the samples with pro-oxidants cobalt (III) acetylacetonate and manganese (II) acetylacetonate. The use of 2 mmol/kg iron (III) acetylacetonate and 4 mmol/kg cobalt (III) acetylacetonate as pro-oxidants gave the highest decrease of elongation at break of the polyethylene foils.

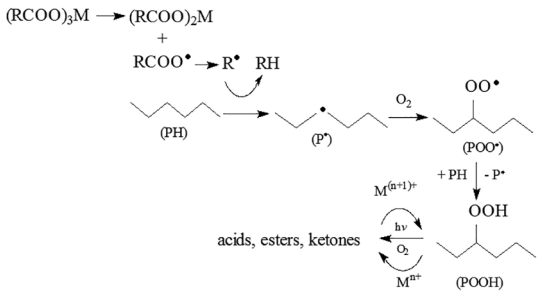
Keywords: *high density polyethylene, pro-oxidants, UV- irradiation, photooxidative degradation, properties*

1. Introduction

Nowadays, a major part of the polymers with regulated service time are photodestructing polymers. To impart the polymers the ability to destruct under light irradiation, special additives are used or light sensitive groups are introduced in their compositions. Owing to the presence of special groups or compounds in them, they decompose under environment conditions to low molecular weight polymers which are then absorbed by the microorganisms present in soil and air.

Since the synthesis of photodestructing polymers containing carbonyl groups in the chain requires certain changes in the synthesis technology, the efforts of many researchers have been devoted to the use of additives as pro-oxidants in the common polymers. Introduced as various complexes, the salts of polyvalent metals accelerate the interaction of polymers with oxygen from the air[1-4] by including oxygen atoms in the polyolefin chains.

The attractiveness of these additives is based on their ability to decompose to free radicals under exposure to light, thus generating additional polyethylene macroradicals. They further react with O_2 to produce hydroperoxides which are the main reason for the destruction of the polymer[5,6]. The last stage is the self-oxidation and breaking of the PE chain[7,8] along classic free radical reactions[9]:



The transition metals possess the unique ability to pass from one oxidation state to another thus catalyzing hydroperoxides destruction[10,11]. They are formed in polymer carcass by the interaction of the polymer with O_2 until free radicals are generated through a cycle of redoxy reactions[12]:

$$ROOH + M^{n+} \longrightarrow RO^{\bullet} + M^{(n+1)+} + OH^{\bullet}$$

$$ROOH + M^{(n+1)+} \longrightarrow ROO^{\bullet} + M^{n+} + H^{+}$$

$$2ROOH \xrightarrow{M^{n+}/M^{(n+1)+}} RO^{\bullet} + ROO^{\bullet} + H_2O$$

The reactions shown above lead to fast accumulation of hydroperoxides and, simultaneously, to formation of oxidation products with low molecular weight[13-16].

The aim of the present work is to obtain photodestructing foils on the basis of high density polyethylene by addition of organic complexes of transition metals as pro-oxidants into them.

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2. Experimental

2.1. Materials

Powdery high density polyethylene (HDPE), product of Lukoil-Neftochim Co., Burgas, Bulgaria, with melting temperature 130°C, melt index 0.16 g/10 min (190°C, 2.160 kg) and density 0.948 g/cm^3 was used for the preparation of the films.

Pro-oxidants: iron acetylacetonate Fe(acac)$_3$ with chemical formula Fe($C_5H_7O_2$)$_3$, melting temperature 180 – 183°C, molar weight 353.17 g/mol and density 5.24 g/cm^3; cobalt acetylacetonate Co(acac)$_3$, with chemical formula Co($C_5H_7O_2$)$_3$, melting temperature 210 – 213°C, molar weight 356.26 g/mol and density 1.43 g/cm^3; manganese acetylacetonate Mn(acac)$_2$ with chemical formula Mn($C_5H_7O_2$)$_2$, melting temperature 248 – 250°C, molar weight 253.15 g/mol and density 1.60 g/cm^3; vanadyl acetylacetonate VO(acac)$_2$ with chemical formula VO($C_5H_7O_2$)$_2$, melting temperature 258°C, molar weight 265.16 g/mol and density 1.50 g/cm^3, all products of Merck, Germany.

2.2 Sample Preparation

The compositions containing 2 or 4 mmol/kg of the pro-oxidants were mixed with HDPE and homogenized in a laboratory mixer (MPW-802, Poland) at 10 s^{-1} for 15 min. The compositions were formed into pellets (because of their low bulk density) and then pressed in a laboratory press PHI (England) between aluminium foils under the following conditions: samples thickness about 400 μm, temperature 190°C, melting period 3 min at 190°C, pressing pressure 22 MPa for 1 min and cooling rate 40ºC/min.

2.3. UV- exposition

The compositions formed as 400 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 35, 60, 90, 150, 250 and 300 h.

2.4. Differential Scanning Calorimeter (DSC) Measurements

The behavior under melting and crystallization in nitrogen atmosphere of samples with mass ca. 4 mg was analyzed using simultaneous thermal analyzer „STA 449F3 Jupiter" (Netzsch, Germany) under the following conditions: first heating from 20 to 200°C, followed by cooling to 20°C and second heating to 600°C at heating rate 12°C/min. The degree of crystallinity of the samples was calculated at $DH_{100\%}$ = 293 J/g for 100% crystalline HDPE[17].

2.5. Fourier Transform Infrared Spectroscopy (FT–IR)

Samples prepared as 25 – 35 μm thick films were analyzed using spectrophotometer produced by "Bruker" (Germany) in the interval 4000 – 400 cm^{-1} with Tensor 27. To estimate the effect of the addition of pro-oxidants on the degree of degradation of polyethylene, the carbonyl index (*CI*) of the samples was determined. It is defined as the ratio of absorbance of carbonyl band around 1717 cm^{-1} and that at 1463 cm^{-1} [18].

2.6. Tensile Properties

The tensile strength, elongation and the other characteristics of the initial HDPE and the foils containing 2 or 4 mmol/kg of the metal acetylacetonates mentioned above were measured on a dynamometer INSTRON 4203 (England) at speed of 50 mm/min and room temperature.

2.7. Melt Index

The melt indices of the initial HDPE and the composition based on it, containing Fe(acac)$_3$, were determined by the MFI (g/10 min) method on an apparatus MFI 3350 Prodemat (France) at temperature of 190ºC and load 2.160 kg.

2.8. Sol-gel analysis

The sol-gel analysis of the initial HDPE and the composition based on it was carried out by extraction with xylene at temperature of 160 – 170ºC.

3. Results and Discussion

The initial temperature of degradation (T_d^i), temperatures corresponding to 10% (T_{10}), 25% (T_{25}) and 50% mass loss (T_{50}), maximum rate of decomposition (T_d^{max})and final temperature of decomposition (T_d^f) of the materials obtained are presented in Table 1. All the samples studied in inert medium were found to have one stage mechanism of destruction despite the UV light exposure duration, contents and type of the pro-oxidants used. The pyrolysis of the initial irradiated HDPE at heating rate of 12°C/min began at 396.4°C and was almost completed at 508.6°C. Similar tendencies were observed for HDPE by other authors, too[19,20]. The shapes of the *TG*- curves for the materials containing organic acetylacetonates of iron, cobalt, vanadium and manganese were also similar. In inert medium, the destruction of non-irradiated HDPE begins at 399.7°C and is completed at 506.1°C. For all the irradiated compositions and these containing Fe, Co, Mn and V acetylacetonates, T_d^i and T_d^f were

Table 1: Temperature characteristics and DSC- thermogram values of the initial, irradiated HDPE and materials based on it with pro-oxidants.

Sample	T_d^i (°C)	T_{10} (°C)	T_{25} (°C)	T_{50} (°C)	T_d^{max} (°C)	T_d^f (°C)	First melting		Second melting		Crystallization	
							T_m (°C)	α (%)	T_m (°C)	α (%)	T_c (°C)	α (%)
Non-irradiated HDPE	399.7	448.4	465.3	478.1	478.0	506.1	128.4	66.9	128.4	66.2	111.5	66.6
Irradiated HDPE	396.4	454.1	466.0	478.8	480.9	508.6	128.5	72.4	127.7	70.8	112.5	67.6
Irradiated HDPE with 2 mmol/kg $Fe(acac)_3$	400.1	452.9	465.4	478.6	480.5	507.5	128.8	71.3	127.3	70.2	112.9	68.1
Irradiated HDPE with 4 mmol/kg $Fe(acac)_3$	406.6	465.2	478.1	486.2	483.7	508.5	128.8	73.1	127.0	71.1	112.3	68.2
Irradiated HDPE with 2 mmol/kg $Co(acac)_3$	403.3	463.1	469.5	481.7	482.8	509.9	128.8	74.9	127.3	73.9	111.9	69.8
Irradiated HDPE with 4 mmol/kg $Co(acac)_3$	407.5	465.4	473.6	482.3	484.9	510.9	128.6	77.1	127.4	75.1	112.2	71.9
Irradiated HDPE with 2 mmol/kg $VO(acac)_2$	400.4	460.0	472.8	483.0	484.0	508.7	129.1	69.0	128.7	72.6	112.5	65.1
Irradiated HDPE with 4 mmol/kg $VO(acac)_2$	399.0	466.0	477.8	483.9	484.4	511.0	129.8	73.3	128.8	68.9	113.1	64.6
Irradiated HDPE with 2 mmol/kg $Mn(acac)_2$	407.0	468.0	472.0	484.0	484.3	510.1	128.6	71.4	127.5	72.5	112.0	70.5
Irradiated HDPE with 4 mmol/kg $Mn(acac)_2$	409.0	467.0	477.0	485.0	484.5	510.4	129.1	72.2	128.3	68.7	112.8	64.0

almost the same as that of non-irradiated HDPE at the heating rate employed and they were found to be in the range 400.1 – 409.0 and 507.5 – 511.0°C, respectively. Comparing the temperatures corresponding to 10, 25, 50% mass loss and T_d^{max} for the non-irradiated and irradiated HDPE foils with these containing pro-oxidants, it can be seen that the temperatures increased by 7 – 20°C. It can be assumed that during the thermal degradation of samples of high density polyethylene in an inert medium occur two competing processes – destruction and recombination. Obtained there from macroradicals probably recombine with each other. Thus, the formed high molecular weight fractions of the polymer require a higher temperature of destruction.

The melting temperatures T_m of the initial non-irradiated and irradiated HDPE, as well as the materials based on it containing Fe, Co, Mn and V acetylacetonates are shown in the same Table 1. For the initial HDPE, the melting temperature is about 130°C and remained unchanged after the addition of pro-oxidants. It means that the UV irradiation had no effect on the T_m of the different samples which is consistent with other publications[21,22]. This is probably related to the predominant attack at the amorphous regions of the samples by UV irradiation.

A tendency of slight increase of the degree of crystallinity α of the samples after first and second melting and crystallization – from 67 to 72% for the initial and irradiated HDPE. The pro-oxidant containing samples showed behaviors similar to these of the initial irradiated HDPE. The degree of crystallinity of $Co(acac)_3$ containing HDPE compositions was slightly higher – up to 75 – 77%. The increased crystallinity is probably due to chain scission in polyethylene macromolecules in their amorphous regions as a result from the photooxidation. This allows for formation of shorter fragments which more easily crystalize in the polymer matrix. It is confirmed by other authors[23,24].

Figure 1 *a* shows the FT–IR spectra of foils from initial and UV irradiated HDPE. The spectrum of the initial polymer has four characteristic bands. The typical bands at 2890 and 2844 cm^{-1} are attributed to the asymmetric and symmetric valent $–CH_2$ vibrations. The peaks at 1463 and 720 cm^{-1} are due to the deformation $–CH_2$ vibrations. Because of the high crystallinity of the polymer (about 70%), the peaks at 1463 and 720 cm^{-1} are split (doublet) and two additional peaks were observed at 1472 and 730 cm^{-1} [25]. It can be seen that the irradiation of HDPE foils resulted in substantial changes in their spectra[26]. The most significant ones were observed in the carbonyl (1700 – 1800 cm^{-1}), amorphous (1300 cm^{-1}) and hydroxyl (3300 – 3400 cm^{-1}) ranges, as well as that around 909 cm^{-1} (due to the unsaturated groups).

The addition of pro-oxidants facilitates the initiation and proceeding of radical reactions and processes of macrochain scission. This leads to formation of free radicals which can further interact with air oxygen to oxidize the polymer. For this reason, the oxidizing ability of the acetylacetonates used was studied by

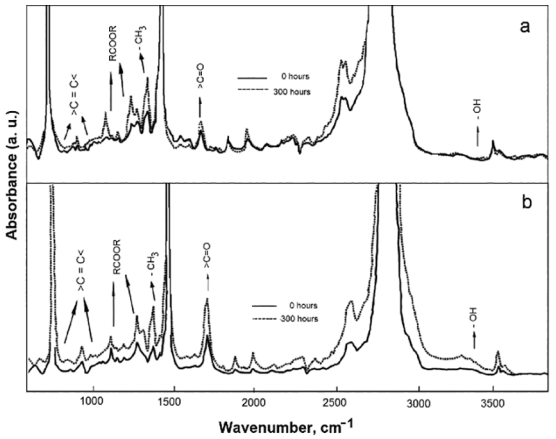

Figure 1: FT–IR spectra of foils of initial non-irradiated (a) and irradiated HDPE containing 2 mmol/kg polymer pro-oxidant Co(acac)3 (b) after exposure 0 and 300 hours

their introduction into HDPE and after irradiation. For both the films of initial irradiated HDPE and the materials based on it containing transition metals acetylacetonates, changes were observed after UV irradiation in all the IR ranges mentioned above. The intensities of these peaks increased as a result from the irradiation (Figure 1 *b*) which proved the formation of various oxidation products[1,12,15].

The better photooxidizing ability of pro-oxidant $Mn(acac)_2$ was proved by the carbonyl index determined. The foils containing this pro-oxidant had 10-11 times higher index than that of the initial HDPE after 35 h irradiation – 0.29 (Figure 2). For the materials containing 2 and 4 mmol/kg polymer $Co(acac)_3$ the carbonyl index increased with the exposure duration with the highest increase being observed with 2 mmol/kg polymer cobalt (III) acetylacetonate – about 7 times. For the materials containing 4 mmol/kg polymer pro-oxidant, however, this property didn't change with exposure and remained slightly higher than that of the initial HDPE. The increase of the carbonyl index for the initial HDPE was negligible even after 60 h UV-irradiation. This is due to the fact that the less branched HDPE have limited permeability for gases and smaller number of tertiary carbon atoms in the macromolecule. Therefore stability of HDPE under oxidation is higher than that of LDPE, as it has been reported[27].

The samples containing $Fe(acac)_3$ showed small increase of the carbonyl index from 0.025 to 0.075. This was due to reactions of chain scission as a result from the photooxidation which lead to formation of fragments of lower molecular weight[28]. The carbonyl index of the foils with $VO(acac)_2$ was also in the range 0.02 – 0.07. The values of this index determined for the $Fe(acac)_3$ and $VO(acac)_2$ foils coincided with these for the initial HDPE despite their concentration in the compositions (Figure 2). This indicates that the use of $Fe(acac)_3$ and $VO(acac)_2$ as pro-oxidants by the photooxidation of the polymer was not effective. It was proved on the basis of the FT–IR analysis that additives of manganese (II) and cobalt (III) acetylacetonates in concentrations 2 mmol/kg polymer are better be used to obtain higher degree of photooxidation.

The photooxidative destruction is most often studied by properties like strength and elongation at break. This is because the process of destruction is

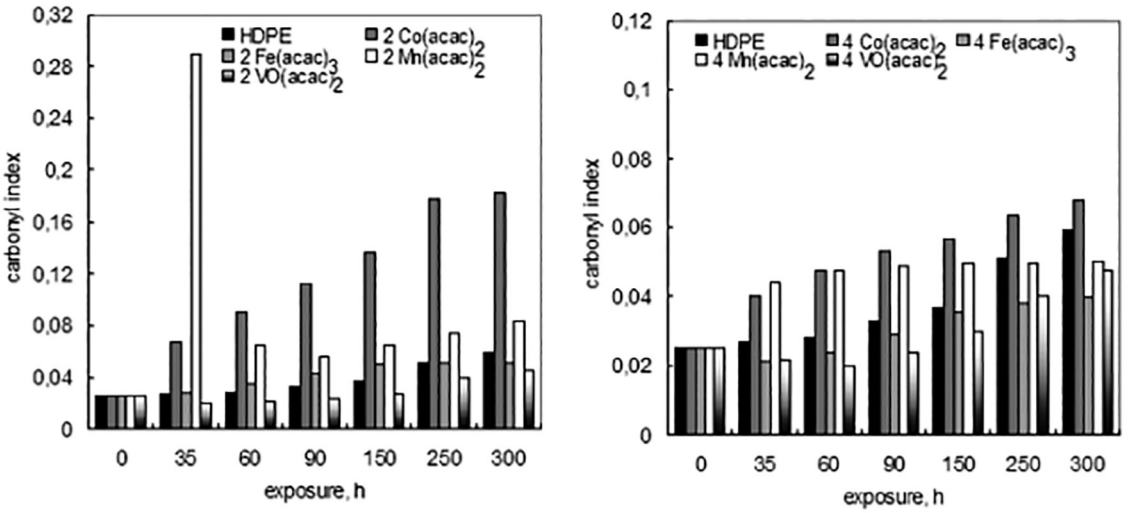

Figure 2: Dependence of the carbonyl index of foils of initial irradiated HDPE and irradiated foils containing pro-oxidants at different exposure times.

related to deterioration of the mechanical properties. These properties are very sensitive to the destruction and provide information on the degree of oxidation of the polymers[27,29]. The decrease of the strength and especially the elongation at break can be related to the decrease of the polymer molecular weight and formation of defects on samples surface inflicted by the UV irradiation.

The dependencies of the strength at break for initial HDPE and the materials based on it containing 2 and 4 mmol/kg acetylacetonates on irradiation duration are presented in Figure 3. Obviously, the initial non-irradiated HDPE had strength 21.6 MPa and it decreased until 60 h irradiation. After that, the strength increased due to processes of cross-linking taking place in the polymer chains. It was confirmed also by the sol-gel analysis carried out and the melt indices of the initial HDPE and the composites based on it. After the irradiation time mentioned above, the samples contained about 8 – 12% gel-fraction and showed melt index in the range 0.07 – 0.10 g/10 min. The cross-linking of HDPE has been proved by other authors, too[30,31].

With the addition of acetylacetonates of transition metals the strength at break decreased to higher extent compared to the initial polymer. The only exception were the compositions containing 2 and 4 mmol/kg polymer $Fe(acac)_3$ for which the strength measured was close or the same as that of the irradiated HDPE. The decrease of the strength of the initial HDPE foils was more pronounced for the samples with pro-oxidants $Co(acac)_3$ and $Mn(acac)_2$ at irradiation durations 35 – 150 h (Figure 3). For the $Mn(acac)_2$ containing foils, it decreased as low as 6 – 7 MPa after 35 h irradiation to reach 5 MPa after 60 h (Figure 3). The polyethylene foils containing 2 and 4 mmol/kg $VO(acac)_2$ as additive accelerating the process of photooxidation, the strength at break decreased. After 60 h UV irradiation it was measured to be about 12 MPa and then gradually increased. The decrease of the strength was due to the decrease of the molecular weight of the polymer matrix – the melt index of the samples was 0.16 – 0.24 g/10 min while for the initial HDPE it was 0.16 g/10 min.

Therefore, the use of $Mn(acac)_2$ and $Co(acac)_3$ as pro-oxidants (especially the manganese (II) acetylacetonate in the concentrations mentioned in the Experimental section) exerted stronger effect on the acceleration of the photooxidative destruction processes taking place in HDPE foils.

The change of the elongation at break on irradiation time for all the samples are shown in Figure 4. It can be seen that the initial non-irradiated HDPE had elongation at break 860%. The samples containing 2 mmol/kg polymer $Fe(acac)_3$ and 4 mmol/kg $Co(acac)_3$ showed faster decrease of the elongation compared to the initial HDPE. The films containing 2 and 4 mmol/kg iron (III) acetylacetonate lost ~90% from their initial elongation after 35 and 60 h, respectively.

The elongation of the foils with $VO(acac)_2$ or $Mn(acac)_2$ also decreased. This tendency is more pronounced for the foils containing 4 mmol/kg $VO(acac)_2$ after 60 h irradiation. The initial HDPE films showed only 25% loss even after 60 h UV irradiation and after 90 h it was about 80 – 90%. The samples of initial HDPE and these containing salts of transition metals could not be tested after 300 h irradiation as they became brittle and collapsed.

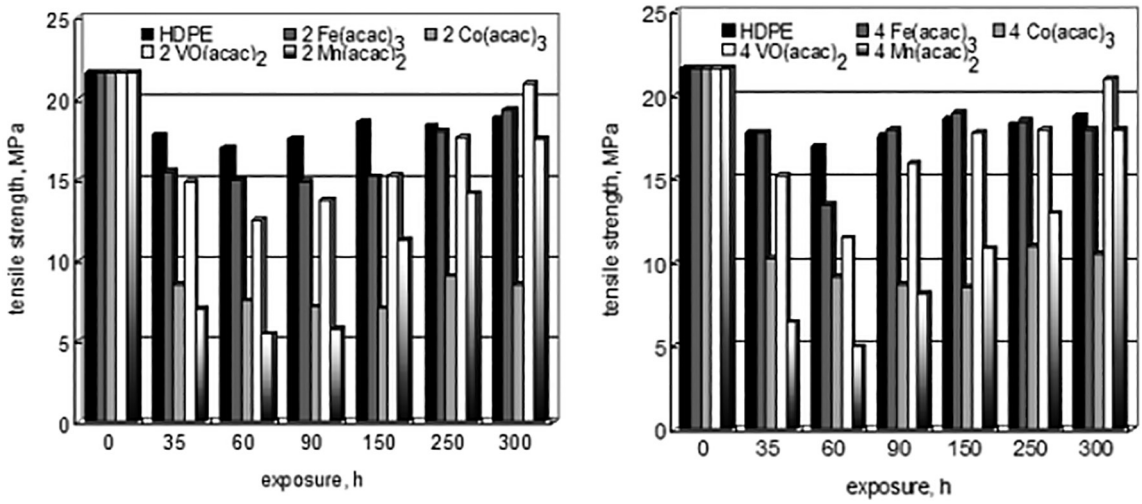

Figure 3: Dependence of the tensile strength of foils of initial irradiated HDPE and irradiated foils containing pro-oxidants at different exposure times

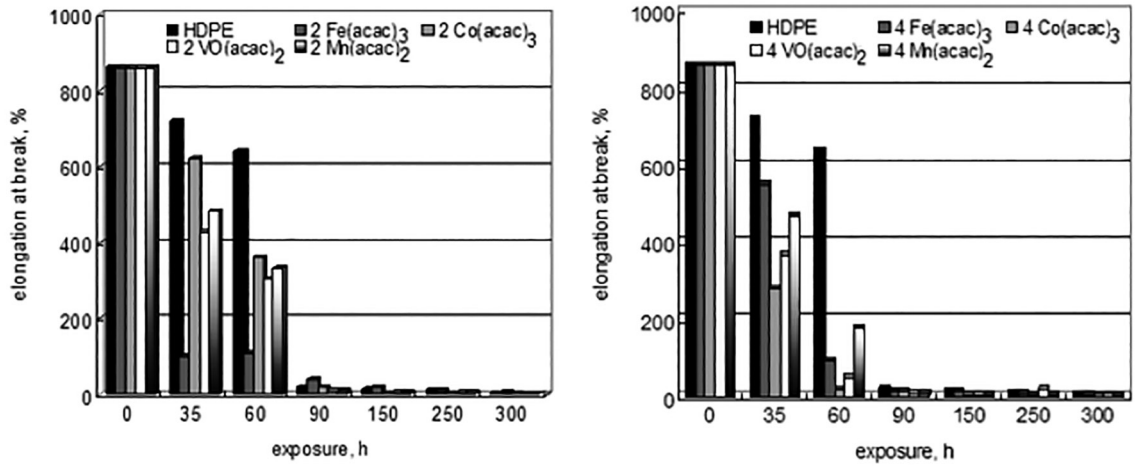

Figure 4: Dependence of the elongation at break of foils of initial irradiated HDPE and irradiated foils containing pro-oxidants at different exposure times.

The highest decrease of the elongation was observed for the HDPE foils containing 2 mmol/kg iron (III) acetylacetonate and 4 mmol/kg cobalt (III) acetylacetonate as pro-oxidants. These results correlate well with the data from the FT-IR spectra.

4. Conclusions

Photodestructing polymers were obtained on the basis of high density polyethylene and acetylacetonate of iron, cobalt, vanadium and manganese. The chemical and physical changes taking place in the samples with or without pro-oxidants after irradiation from UV source were analyzed. The effect of the acetylacetonates specified on the processes of photodestructive oxidation of the polymer was studied. It was found that by their activity to oxidation the above mentioned pro-oxidants can be arranged in the following order: $Mn(acac)_2 > Co(acac)_3 > Fe(acac)_3 \approx VO(acac)_2$. This shows that the organic complexes used are suitable as additives accelerating the process of photooxidative destruction of high density polyethylene foils.

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