Influence of cobalt stearate on destabilization of high-pressure polyethylene

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Abstract

Introduction. The main purpose of research is to provide a timer-based polymer composition of high pressure polyethylene and cobalt stearate, which starts self-destruction through a certain period of time and can be used in the production of mini-packets for packing food products in supermarkets and further reduce environmental pollution.

Materials and methods. To determine the technological parameters processing of the compositions were performed thermomechanical and differential thermal analysis of cobalt stearate. To assess the destabilizing impact of cobalt stearate in the mixture held in the timer determination shrinkage conditional strength and elongation, getting dry residue by dissolving in xylene and water absorption. Infrared spectroscopy was used to assess the destabilizing effect on the molecular level.

Results and discussion. In determining the properties of cobalt stearate the thermomechanical curve confirmed by the plateau crossing from the pseudo-crystalline to the amorphous state. Analysis was conducted with next parameters: starting temperature measuring 16.8° C, weighed material - 24.1 mg, the sensitivity of apparatus - 20mg, rising of temperature 10 ° / min, weight loss after full cooling oven 85.5 %, the decomposition start temperature - 200°.

The optimal concentration is area of 3% in which the shrinkage of film sample was 46%, the value of the conventional longitudinal strength decreases after 3 months of exposure, corresponding to the climate zone of central Ukraine. After dissolving samples in xylene percentage of lost mass was 99.74%, which is a comparative characteristic for assess the depth of degradation chains. In determining of water absorption, the maximum exposure available for next investigation is 8 hours, at which water absorption is 21.4%. Infrared spectroscopy with increasing irradiation time gives the highest rate of ketone groups formation (in the range 1710-1725 см$^{-1}$), alcoholic groups (1150 см$^{-1}$) and a significant increase in the amount of water adsorption (3360 см$^{-1}$) at a concentration of cobalt stearate within 3%, which also demonstrates depth of chains degradation on molecular level.

Conclusion. The timer-based polymer composition based on high-pressure polyethylene and cobalt stearate is designed with maximum efficiency in the area of 3%, proved its effectiveness and efficiency.

Introduction

The disposal of trash is a problem confronting our society [1]. Our available landfills are becoming exhausted. While polymers compose only about 8% by weight (20% by volume) of landfills [2], there is much focus on polymer accumulation because of their high visibility [3]. Recycling is one of the most important actions currently available to reduce these impacts and represents one of the most dynamic areas in the plastics industry today [4]. But recycling requires additional financial investments, moreover, to gather footage for a film packaging recycling extremely difficult. The article considers specifically film packaging materials for packing food and nonfood products, the most common of them - mini-packages for supermarkets. Therefore, the main goal is to create efficient polymer compositions based on high-pressure polyethylene and cobalt stearate, which is influenced by environmental factors (UV radiation, temperature, humidity) would break down after a specified period of time and not be a threat for environment.

Materials and methods

To determine the technological parameters processing of the compositions were performed thermomechanical and differential thermal analysis of cobalt stearate. To assess the destabilizing impact of cobalt stearate in the mixture held in the timer determination shrinkage conditional strength and elongation, getting dry residue by dissolving in xylene and water absorption. Infrared spectroscopy was used to assess the destabilizing effect on the molecular level.

Compositions. Compositions, used for getting samples are presented below (Table 1).

Table 1

Compositions used for samples

Component	Concentration C, %					
	1	**2**	**3**	**4**	**5**	**6**
LDPE 15803-020	100	99,9	99,5	99	97	95
Cobalt stearate	0	0,1	0,5	1	3	5

Getting of film samples. The hopper is filled by prepared composition comprising of high pressure polyethylene stamps 15803-020 and cobalt stearate. Preparation of the composition of dry components was conducted immediately before loading into the extruder to avoid excessive moisture environment and stratification. Samples were got by hot-melt extrusion [6], [7].

Firstly, preparation of composition was planed by method of dressing polyethylene granules and powdering them by cobalt stearate [11]. But after research, it became clear that because of relatively low compared to the polyethylene melting point of cobalt stearate serves as dressing himself, that is an additional component that would carry out the same function, such as paraffin or stearin simply not needed [8]. In addition, the additional component would increase the content of low molecular weight fraction, ie, reduced density to melt.

By varying the concentration of cobalt stearate received film with different its containing, ranging from 0 to 5% in polymer matrix.

Formation of the film is due to air supply, cooling intensity and speed of pulling rolls receiver.

Main specifications of installation:

The diameter of the worm, mm - 90

Rim Diameter, mm - 220

Dorn diameter, mm - 75

The size of the gap forming, mm - 1

The extent and degree of stretching blow are important parameters of the formation process, since their change can be obtained isotropic and anisotropic film, improve physical and mechanical properties of the film.

Table 2

Technological parameters of the process of obtaining blown film based on LDPE compositions

Compositions / Parameters	Values				
	1	2	3	4	5
Temperature, °C: Loading zone First worm zone Second worm zone Circular zone Head	60 120 160 180 180				
Rotational speed of worm n, turn/min	15				
Tension on anchor, V	220				
Current strength worm drive, A	19	15	17	17	18
Productivity G, kg/h	7,78				
Admission speed film V, m/min	2,8				
The width of sleeve, mm (with an allowance,%)	235 ± 2	280 ± 2	235 ± 5	230 ± 5	230± 5
Blow degree, %	179	194	191	191	191

Periods of exposure. Based on data from NASA, the average intensity of irradiation latitude in which the Ukraine is 3,2 kW / day.

Average radiation intensity is:

$$3,2 \cdot 1000 \cdot 365 = 1168000 W / year$$

Just as in the lab are available two lamps, 400W and 1000W intensity calculation is provided for both of them.

Lamp intensity 400W, imitates UV-radiation in the environment for 121,67 hours.

To simulate the exposure duration of month it will need 10h:

$$\frac{121,67 \cdot 30}{365} = 10h$$

Therefore, selected for the study intervals 1,2,3,4,5 months of this lamp imitates 10, 20, 30, 40 and 50 hours of exposure.

Based on the fact that the lamp of 1000W intensity is 2,5 times stronger, it was decided to use it. This lamp simulates intervals 1,2,3,4,5 months at 4, 8,12, 16 and 20 hours exposure equivalent climate zone of central Ukraine. Thus, the characteristics of the film used to package introduced mandatory property - degradation term.

Results and discussion

The impact of cobalt stearate on destruction of polyethylene macro – chains. The feasibility of using it except prevalence (widely used in rubber, tire production) and economic accessibility as a catalyst for action photoaging.

Under the influence of UV-rays and provide additional energy, the least strong link ~Co - O~ rushes and formed active macro-radical chain begins to break down polyethylene.

In this process is a photochemical degradation (photolysis) caused by light and caused cobalt stearate [9]. During photolysis, takes place not only breaking apart chemical bonds but also stitching, double bonds and formation of free radicals. The process is characterized by the quantum yield gaps chain (number of breaks per absorbed quantum of light), which for various polymers is in the range of 10^{-4}-10^{-1}. Because of the high concentration of free radicals in relatively small areas, the destruction is accompanied stitching macromolecules, sometimes above the prevailing destruction.

The first stage is formation of macro-radical. In the case of cobalt stearate, stearin anion pulls over the electron density and thereby develops the double bond thus formed macro-radical.

$$-CH_2-CH_2-CH_2-CH_2- \rightarrow -CH_2-\overset{\bullet}{C}H_2+\overset{\bullet}{C}H_2-CH_2-$$
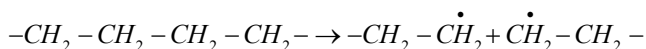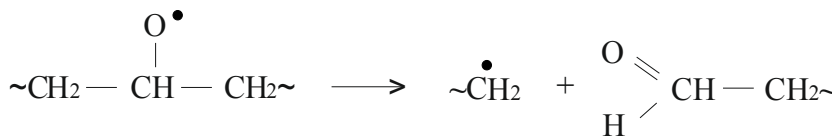
Further, the same processes as in the thermal destruction can proceed in the polymer. Since breaking the chain already held, begins its further growth:
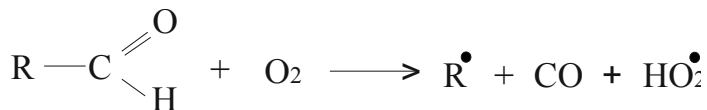
$$R^{\bullet}+O_2 \rightarrow RO_2^{\bullet}$$
$$RO_2^{\bullet}+RH \rightarrow ROOH+R^{\bullet}$$
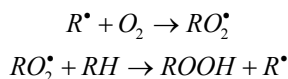
In addition, the influence of $RO^{\bullet}$-radical can also be described by the following mechanism:
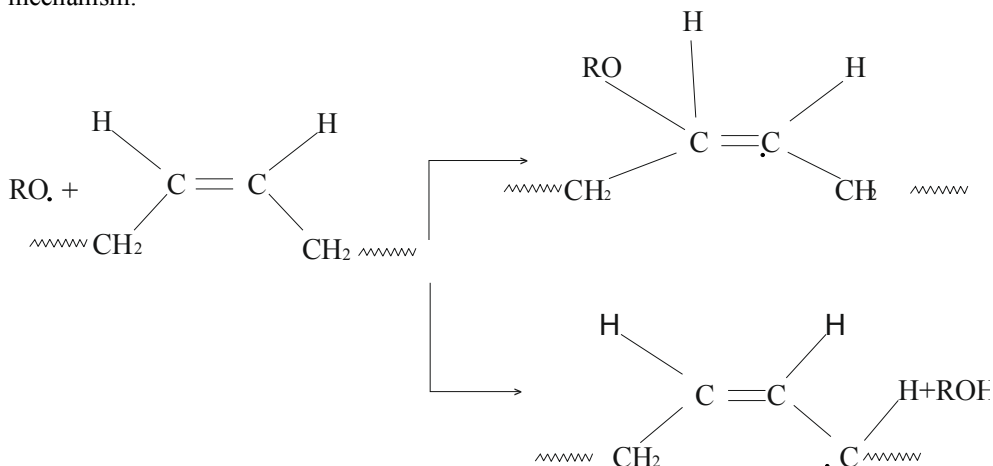
In parallel form macromolecular compounds. $RO^{\bullet}$-radicals can further decompose scheme that is below.

$$\text{~CH}_2 \!-\! \overset{\overset{\displaystyle O^\bullet}{|}}{CH} \!-\! CH_2\text{~} \longrightarrow \text{~}\overset{\bullet}{CH}_2 \; + \; \overset{O}{\underset{H}{\diagdown}}\!\!CH \!-\! CH_2\text{~}$$

Aldehyde group, continue being oxidized:

$$R \!-\! C\overset{\diagup O}{\diagdown_H} \; + \; O_2 \; \longrightarrow \; \overset{\bullet}{R} \; + \; CO \; + \; H\overset{\bullet}{O_2}$$

The thermo-mechanical and differential thermal analysis of samples. In determining the properties of cobalt stearate by differential thermal method the thermomechanical curve confirmed by the plateau crossing from the pseudo-crystalline to the amorphous state. In view of the state of solid cobalt stearate it suggests about the crystal structure as well as broken, when force is applied, having a straight edge chipping and shine. Upon reaching a plateau, it is clearly evident that the material is amorphous. By analysis which was conducted with next parameters: starting temperature measuring 16.8° C, weighed material - 24.1 mg, the sensitivity of apparatus - 20mg, rising of temperature 10 ° / min, weight loss after full cooling oven 85.5 %. The curve shows exo-effect of sample with increasing temperature. Up to 200° C temperature observed slow "soft" growth of curve corresponding to undermine the falling mass. This trend is explained by the foaming material through the device because of the high sensitivity captures the seeming increase in mass of the sample. At 200° C the beginning there plateau, which at the value of 250° C passes in a fairly sharp rise in the curve is falling value of the mass. This temperature clearly shows that sample starts to burn and decompose. In the range of 300° C-500° C is thermal expansion of the material. The highest peak accounted on 450° C, which corresponds to the point in which the process takes place with the greatest activity. Waves on the curve in the temperature range 550° C-950° C can be explained in two points. The first is high sensitivity equipment that captures noises. The second is the possibility of moving to another sample verifiable modification.

Determination of shrinkage. Higher concentrations of cobalt stearate reduces the shrinkage. This phenomenon can be explained by increased yield strength, as evidenced by the fall amperage anchored motor. Since the viscosity dropped, then the molecules forming the sleeve easier sliped relative to each other and to a lesser degree there was swing the sectors degree of orientation is reduced as the confirmed results of the study on shrinkage. Growth values the importance shrinkage 5% * explains the presence of quite large particles of cobalt stearate, visible to the naked eye, which are centers of concentration of stress.

Determination of relative strength and elongation. Research carried out in each group concentrations of cobalt stearate and over time during irradiation. The starting point was to compare the strength characteristics for each value of the concentration of cobalt stearate to radiation. The lowest values observed at concentrations of 0.5% and is accompanied by a sharp drop in viscosity.

That is, changing the viscosity and thermal characteristics. At constant cooling conditions, the drop of viscosity caused displacement crystallization line. Since the distance

to the line of crystallization decreased, it resulted in underdevelopment crystallite structure, which led to a lower value of relative strength compared to other models.

In each of the exposure period is compared between samples with different concentrations of cobalt stearate. A comparison of the graphs shows that the most destructive action endowed is area of concentration 3%. This concentration is optimal. Optimum results from the fact that up to 3% cobalt stearate in the composition is escalating destructive properties.

As said before, the samples obtained by the same parameters with the concentration of 5% are not accepted for investigation, because so much of cobalt stearate gives a high volume of bubbles. This model does not reflect the real picture of strength characteristics.

Instead, the samples with the same concentration of cobalt stearate, but produced at lower turns were used. With increasing exposure time, sample with concentration of cobalt stearate 5% yield samples at 3%, because firstly, for such a large number of accumulted radicals, as in samples with a concentration of 5%, beginning the process of crosslinking, and secondly, visible to the naked eye stearate cobalt particles in the thick film perform function of reinforcing the principle of reinforcing particles.

Determination dry residue dissolving in xylene. Film samples with concentrations of cobalt stearate 0.1, 0.5, 1, 3, and 5% were obtained following dependence.

The graph in Figure 1 clearly shows that over time, the strongest fall observed in the weight value once the concentration of cobalt stearate 3%, due to the most intense destruction of macro-chains for the concentration.

There is a complete dissolution of the sample with the concentration of cobalt stearate 3%, indicating the deepest in this number of samples degradation of the polymer chains.
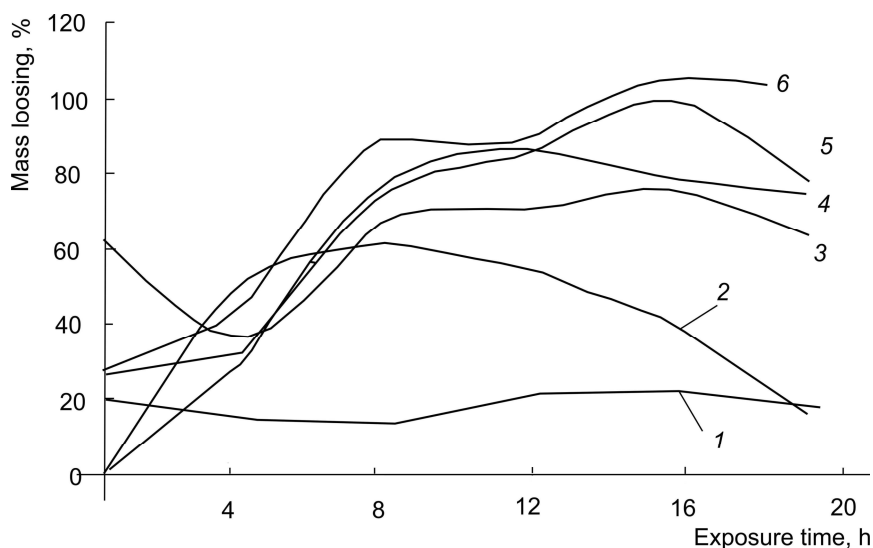

Fig. 1. Dependence of weight loss in dissolving in xylene for pure PE and cobalt stearate contented. Concentrations are 1 – 0%, 2- 0,1%, 3 – 0,5%, 4 – 1%, 5 – 3% and 6 – 5%.

Determination of water absorption. For comparison, in each row exposure time, studied a sample of pure PE films.

Speaking about the most effective concentration of cobalt stearate 3%, the graph presented in Figure 2 shows that in times of irradiation 8-16 hours, water absorption is reduced, as well as in most of the samples which could be explained by the phenomenon of crosslinking, which also initialized UV-radiation [12],[13]. This analysis allowed to determine not only the amount of water absorbed, indicating the degree of degradation of the polymer chains, but also clearly see the influence of moisture in the environment to your samples. Since moisture is an additional natural factor and affect sent to landfill mini package with UV radiation, no harm will see qualitative changes in the samples [10].
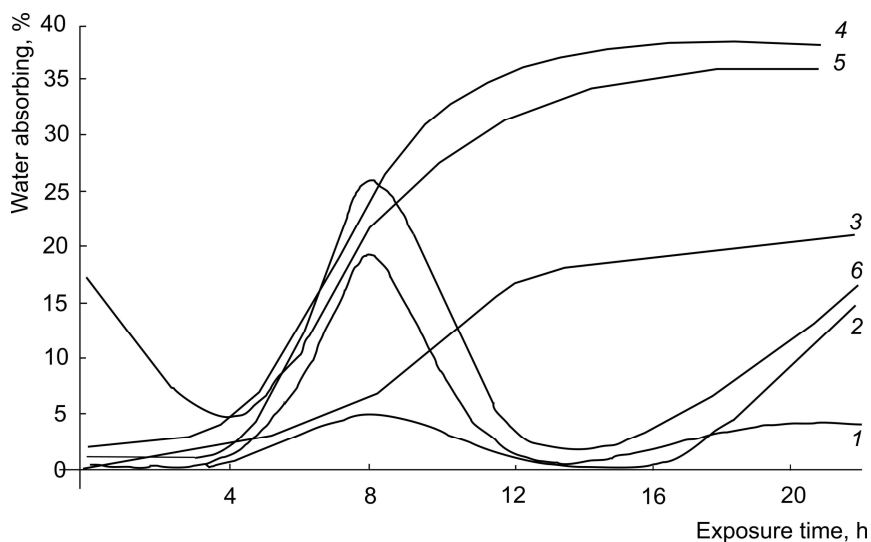
Fig. 2. The dependence of water absorption of the exposure time for pure PE and cobalt stearate contented. Concentrations are 1 – 0%, 2- 0,1%, 3 – 0,5%, 4 – 1%, 5 – 3% and 6 – 5%.

After the moisturising, some samples were not possible to weigh because of the fact that they are almost completely dispersed or dissolved. The most effective concentration is 3%.

Infrared spectroscopy. Figure 3 shows the infrared spectrum of the film of pure PE. It is characterized by peaks is in the range of 2930 cm^{-1} to 2840 cm^{-1}, corresponding to oscillations of group CH_2 (assym) and heart failure, as well as peaks in 1460 cm^{-1} (δCH_2), 1365 cm^{-1} (δCH_2) and 710 cm^{-1} (γCH_2).

Significant changes in the internal structure of samples with a concentration of 3% cobalt stearate can be seen already after 4 hours of irradiation under UV. There was a big peak in the area of 1710-1725 cm^{-1}, indicating the formation of ketone groups. Ketone groups show that the dissolved polymer chain really started to attach oxygen. In addition, the area of 1150 cm^{-1} peak seen characterizing the alcohol group C-O, which also shows the lipid chains with torn ligaments. As a result of shorter chains, increased water sorption content in the sample.
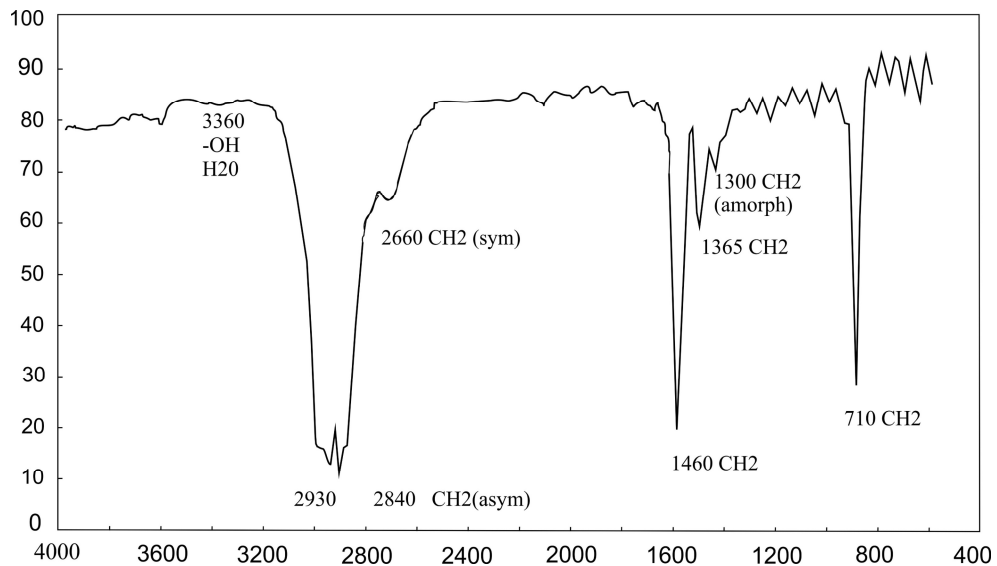
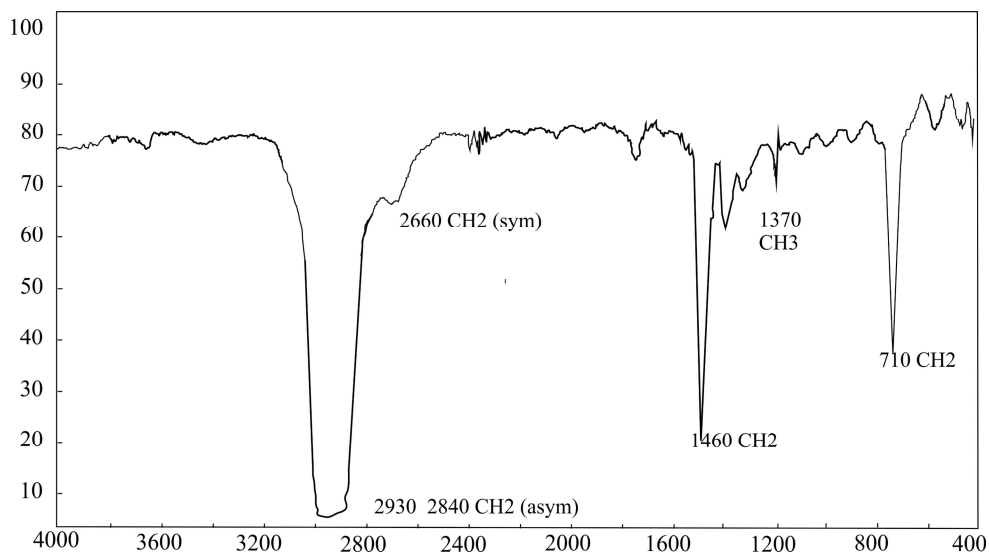**Fig. 3. Infrared spectrum of pure PE films**

Fig. 4. The infrared spectrum of the film containing 0.1% cobalt stearate without irradiation
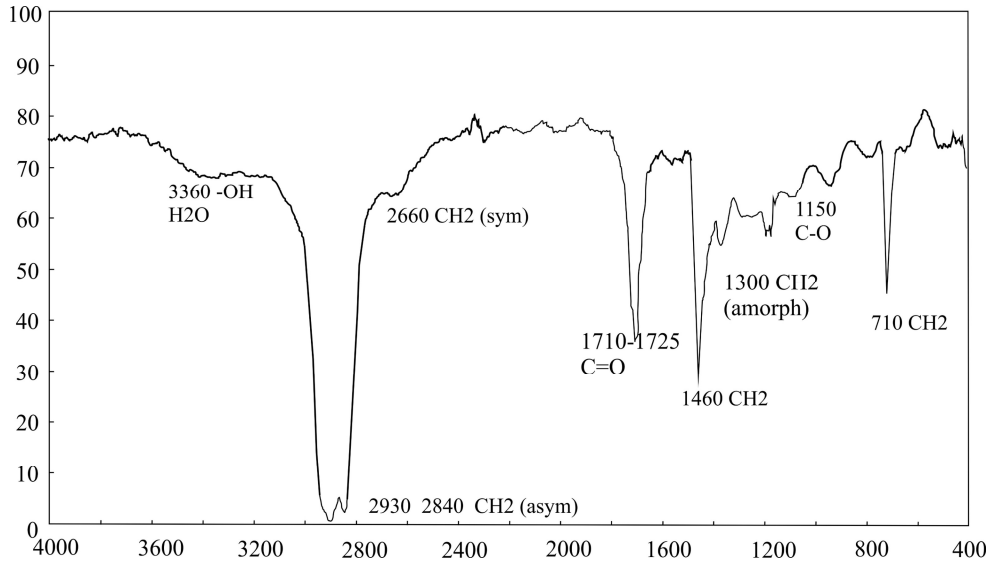
Fig. 5. The infrared spectrum of the film containing 3% cobalt stearate after 4 hours of exposure
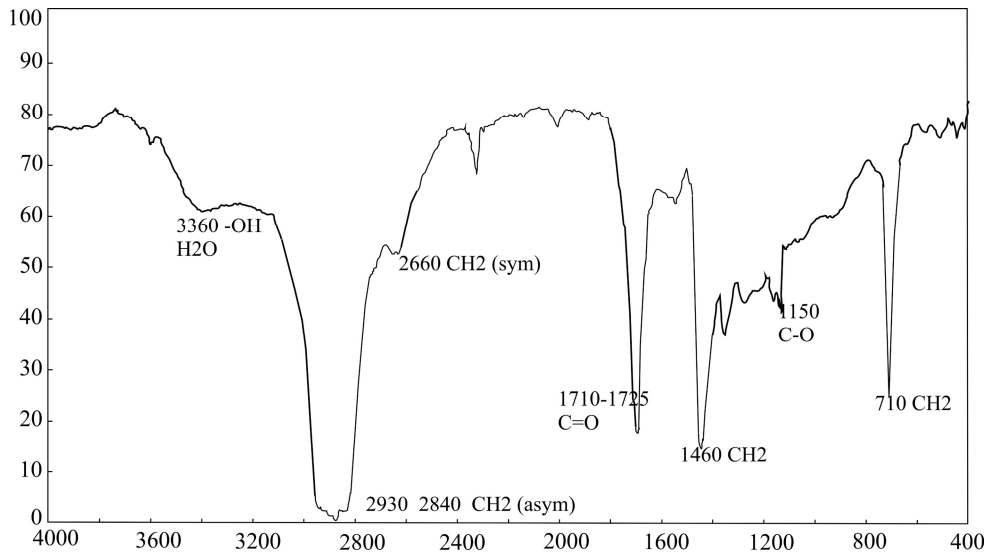

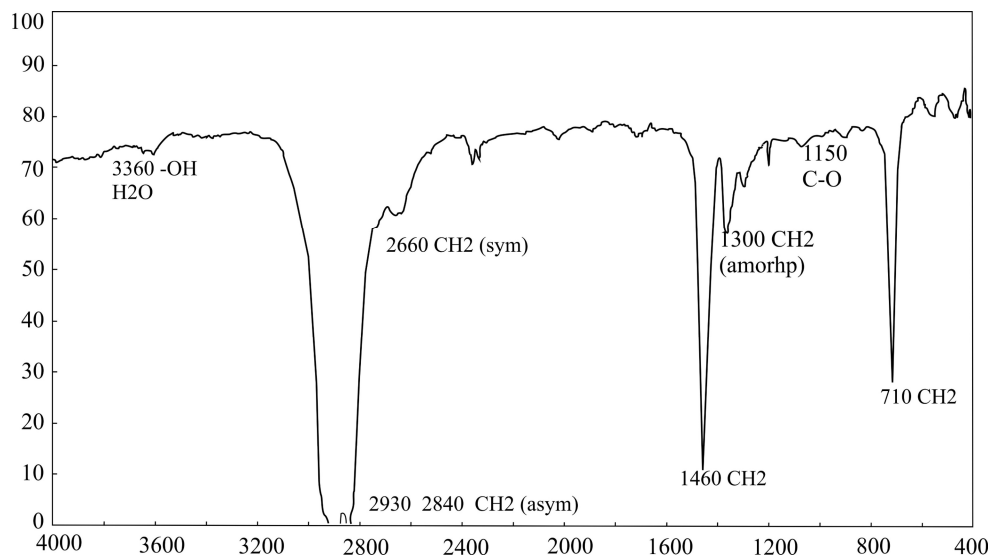**Fig. 6. infrared film containing 3% cobalt stearate after 8 hours irradiation**

Fig. 7. The infrared spectrum of pure PE films after irradiation for 8 hours
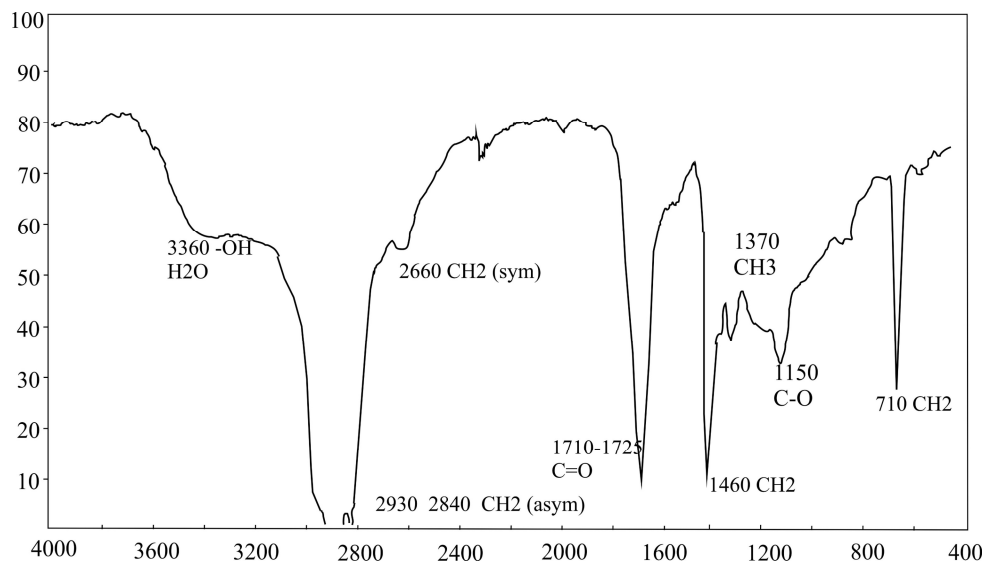

Fig. 8. infrared film containing 3% cobalt stearate after 12 hours of exposure
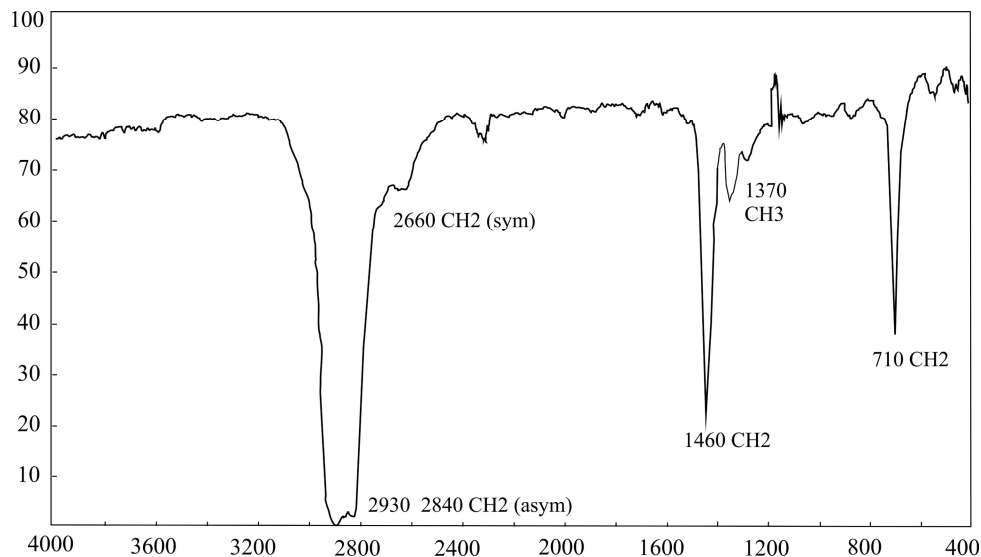
Fig. 9. The infrared spectrum of pure PE films after 12 hours of exposure

Comparing film samples without filling stearate cobalt and filled with cobalt stearate with concentration of 3% after exposure for 12 hours, conclusions can be done. Over time, deeper 1710-1725 cm^{-1} peak in the area, indicating that the increase in ketone C = O groups and deepening oxidizing of chains. In addition, the peak in 1150 cm^{-1} zone was deepened in, that of alcohol, which is oxidized one end of the chain, accumulate over time.

Data of Infrared spectroscopy clearly show that cobalt stearate percentage in area of 3% actually works as destabilizing additive that promotes oxidation and degradation of polymer marco-chains.

Conclusion

The timer-based composition based LDPE and cobalt stearate at maximum efficiency in the neighborhood of 3% concentration is developed, proved its effectiveness and efficiency. In this part of the composition there is a profound degradation of the polymer chains that proved complex of analyzes, which simulated use of the product for the purpose of the film, and after that - the impact of environmental factors.

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