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Oxo-degradation of LDPE with pro-oxidant additive

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Abstract. The article describes polymeric additives accelerating the thermal oxidation of polyolefins at moderate temperatures (oxo-degradation additives), which increase the ability of polyolefins to oxo-decomposition. The oxo-degradation additive includes metal-supported 2-ethylhexanoates or mixtures of metal 2-ethylhexanoates supported on an inert carrier.

1. Introduction

At present, the population of large cities is facing an acute problem of giant landfills for municipal solid waste (MSW) [1]. Most of the MSW is polymeric waste due to its short service life (for example, as a packaging material) and high resistance to environmental factors. So far separate collection of garbage has not found due attention, which would have more effectively solved the problem of recycling and facilitating the disposal of solid waste.

To partially solve this problem, biodegradable polymers are developed [2-4], as well as additives that accelerate the decomposition of polymeric wastes (for example, polyethylene) due to the destruction of long polymer chains under the influence of natural factors such as heat, moisture, light and microorganisms.

To make materials from polyolefins (polyethylene and polypropylene) the ability of biodegradation one of the way is the introduction of natural filler. The resulting material is capable of destructuring in environmental conditions after the expiration of the service. On the other hand the introduction of natural filler reduces the cost of the material as a result of the replacement of the polymer matrix, derived from non-renewable raw materials. It should be noted that in this direction of creation of biodegradable polymer materials, the use of cheap non-nutritive or feed value materials and production wastes is most promising. Thus, to increase the rate of biodegradation, polyolefins are introduced into: cellulose, starch, wood, soy flour rice husks, etc. [2-8].

Another way of giving biodegradability to polymeric materials based on polyolefins is the introduction of pro-oxidant additives into the polymer matrix, which contain oxidation initiators [9, 10]. Due to their presence as a result of the action of light or heat, the oxidation of the polymer matrix is initiated. The ongoing chemical processes contribute to the destruction of polymer macromolecules, the accumulation of oxygen-containing groups, the decrease in molecular weight and the fragmentation of the entire material. The most widely used as oxo-decomposing additives are stearates of transition metals. Despite their wide distribution, their main disadvantage is the low content of metals of variable valence relative to the weight of salt. To solve this problem, we proposed using metal 2-ethylhexanoates as their pro-oxidants (their acid residue is almost two times less).



2. Experimental part

2.1 Getting the pro-oxidant additive

The pro-oxidant additive is a variable-valence metal salt deposited on an inert carrier (calcium carbonate) (metal 2-ethylhexanoates). As a 2-ethylhexanoate of metals and their mixtures used sikkativy company LLC "INDLAC", which are solutions of individual salts or their mixtures in Nefras - C4 - 155/200. Calcium nanocarbonate (particle size 70 - 90 nm), obtained by grinding on a ball mill of calcium carbonate brand Omyafilm 750-KA from Omya Madencilik A.S., was thoroughly mixed with a salt solution or a mixture of salts in Nefras - C4 - 155/200 to obtain a homogeneous pasty mass. The resulting mass was dried at a temperature of 90 ° C for 24 hours until complete removal of the solvent and crushed to obtain a homogeneous powder crumbly (80-100 nm).

2.2 Getting the masterbatch

A masterbatch was obtained by mixing polyethylene (LDPE of 15803-020 grade (PJSC Kazanorgsintez) with an oxidation initiator in a Brabender-type laboratory mixer for homogenization at 140 ° C, the number of revolutions is 20-30 rpm, the total residence time of the mixture in the mixer chamber is 6 minutes. The resulting mixture was cooled to room temperature, crushed to crumb. The obtained oxo-decomposing thermoplastic additive can be used as an additive to polymer compositions based on polyolefins (polyethylene) or their copolymers. The recipient of the masterbatch: LDPE (50 wt.%), inert carrier (calcium carbonate) 40 wt.%) metal salts of variable valence (2-ethylhexanoate cobalt - 1.9 wt. %, zinc - 2.8 wt.% and zirconium - 5.3 wt.%)

2.3 Getting the base polymer with the addition of masterbatch

The content of masterbatch in the base polymer 1 and 3 wt. % The calculated amount of the base polymer was loaded into a Brabender type laboratory mixer (20–30 rpm) at 140–2 ° C, then the required weight of masterbatch prepared as described above was added and mixing continued until the mixture was homogenized (6–8 minutes).). The composition of the base polymers prepared with the addition of masterbathe, are presented in table 1. The material was cooled to room temperature, Production of film samples

Table 1. Recipe base polymers prepared with the addition of masterbatch

№ blend	Content of component, wt. %	
	LDPE	Masterbatch
1	100	-
2	-	100
3	99	1
4	97	3

2.4 Preparation of films

Samples of films with a thickness of 80–100 µm were obtained by pressing on a laboratory press at T = 140 ° C, time 60 seconds, pressure 50 kgf / cm².

2.5 Research methods

By the method of IR Fourier spectroscopy, the accumulation of carbonyl groups D_{1720}/D_{3640} was estimated. The optical band at 1720 cm⁻¹ corresponds to carbonyl groups, the accumulation of which indicates the oxidation process of the samples under the experimental conditions. The optical band at 3640 cm⁻¹ is an internal standard for LDPE samples; reference to it makes it possible to exclude the effect of the sample thickness on its IR absorption spectrum [11]. Spectrometric studies were carried out using the equipment of the Collective Use Center "New Materials and Technologies" " at the Emanuel Institute of Biochemical Physics of

Russian Academy of Sciences, Perkin Elmer Spectrum 100, at $T = 23 \pm 2$ ° C in transmitted light in the wavelength range $4600 \leq \nu \leq 450$ cm⁻¹.

In order to identify the strength characteristics of the obtained mixtures were conducted physical and mechanical tests in a laboratory tensile machine PM-10. Testing, training and payment module samples were assayed according to GOST 9550-81.

3. Results and discussion

Structural changes during degradation were investigated by recording FTIR spectra of films as a function of degradation time.

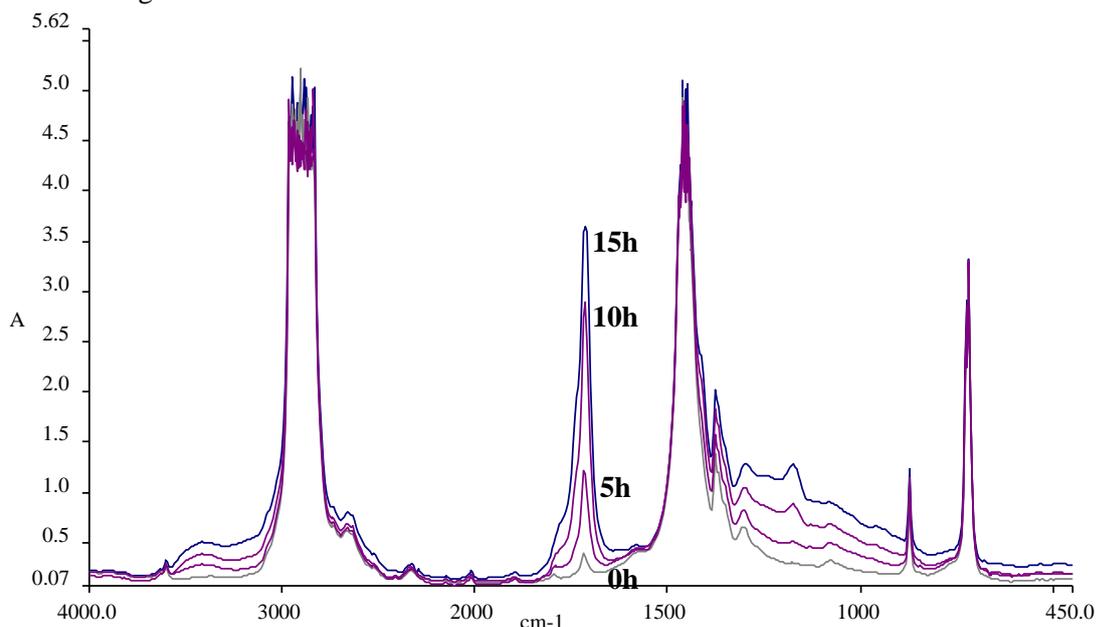


Figure 1. FTIR spectra for LDPE with 3% masterbatch during degradation.

A sharp increase in IR absorption in the carbonyl region ($>C=O$, between 1800 and 1650 cm⁻¹) was detected with exposure time in all samples containing pro-oxidant additive (as an example, FTIR spectra for LDPE with 3% masterbatch during degradation Figure 1). This region corresponds to different oxidized products, such as carboxylic acids (1708 - 1698 cm⁻¹), ketones (1723 - 1713 cm⁻¹), aldehydes (1740 - 1733 cm⁻¹) and lactones (1786 - 1780 cm⁻¹) [12-14].

Figure 2 shows kinetic curves of degradation for LDPE at different aging times and for masterbatch and LDPE with 1 and 3% masterbatch. As can be seen from the figure 2, materials containing pro-oxidant additive in their composition are easily oxidizable compared with polyethylene without additives (curve 1). As was to be expected, an increase in the number of ORDs in polyethylene accelerates the process of oxidation. However, it should be noted that the oxidation curve of the oxo-destructive additive itself lies between the oxidation curves of LDPE + 1% MB and LDPE + 3% MB. Apparently, this is due to the high concentration of inert carrier in the superconcentrate, which prevents the oxidation of LDPE in it.

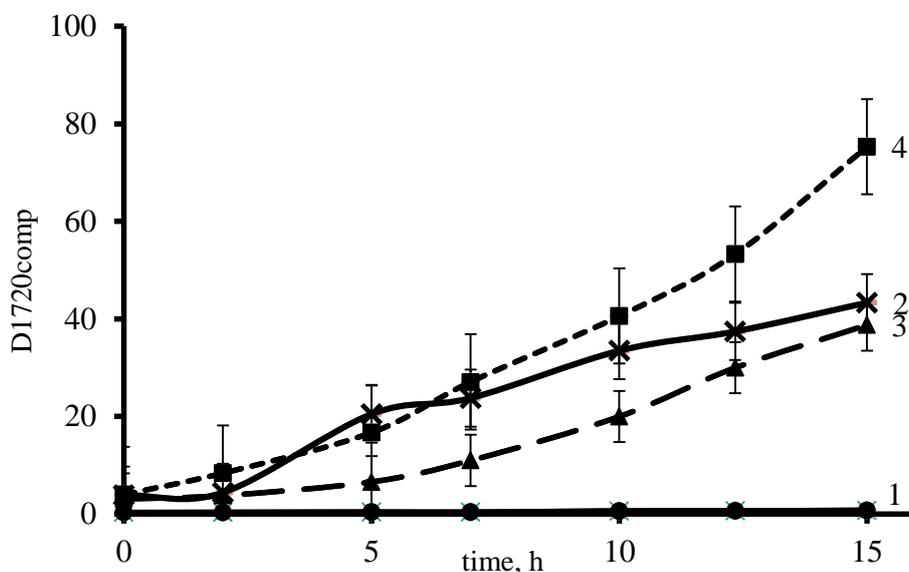
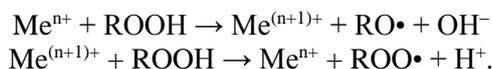


Figure 2. Dynamics of D1720otn changes during thermal oxidation of base polyethylene samples with the introduction of masterbatch (MB), where 1 - LDPE, 2 - MB, 3 - LDPE + 1% MB, 4 - LDPE + 3% MB.

It is well known that thermooxidative destruction of polyethylene proceeds by a free radical mechanism similar to the oxidation of low molecular weight hydrocarbons [15]. Polyethylene films subjected to thermal aging, containing prooxidant additives, demonstrate a higher level of oxidation, which is fixed by an increase in the number of carbonyl groups in the IR spectra. The presence of metals has a catalyzing effect on the oxidation processes due to the occurrence of redox reactions [16, 17]:



The resulting radicals can react with the macromolecules of the polymer to form carbonyl groups, which lead to the breaking of the chain of macromolecules, followed by embrittlement and fragmentation of the polymer material.

Thus, the use of metal 2-ethylhexanoates as initiators of oxidation for polyethylene makes it possible to accelerate polymer degradation processes in the environment, increasing its availability to microorganisms by reducing the molecular weight, increasing the hydrophilicity of the material (accumulation of oxygen-containing functional groups) and fragmentation of the material.

Conventional tensile testing was performed as indicated in the experimental section. Destructive stress under tension and relative extension were used to monitor mechanical changes in the material under with the introduction of masterbatch into the LDPE.

From the results presented in the table 2 it follows that the physico-mechanical characteristics of the film materials of pure LDPE and containing prooxidants in their composition have similar values.

Table 2. Physico-mechanical characteristics of film samples

№ blend	Destructive stress under tension, MPa	Relative extension, %
1	20	320
2	-	-
3	20	322
4	19,5	319

The tensile properties of LDPE containing Oxo additives without any exposure to degradation conditions were identical to the properties of neat LDPE. Therefore, the Oxo additives did not degrade the polymers during the processing stage and did not cause any noticeable structural changes in the LDPE.

4. Conclusion

Thus, as a result of research, it has been shown that polymeric materials containing pro-oxidant additive (2-ethylhexanoates of cobalt, zinc, and zirconium) in low concentrations demonstrate a higher level of oxidation compared to polyethylene. The presence of 2-ethylhexanoates of cobalt, zinc and zirconium leads to an increase in the concentration of carbonyl groups in the polymer material during the thermoaddition process and, as a consequence, to an increase in polarity and adhesion characteristics of the surface, which increases its accessibility to the action of microorganisms. It should be noted that to use this masterbatch as a commercial product, it is necessary to introduce oxidation stabilizers to prevent premature aging of the material during its storage and operation.

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