Biodegradation of polymer compositions with pro-oxidants

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Abstract. Oxo-biodegradable plastics are widely used as an alternative to well-known polyethylene and polypropylene. Thanks to the polyolefin base, they have the necessary set of operating characteristics and are able to be processed with the same parameters as for example polyethylene. The presence of prooxidant in their composition ensures its o xo-destruction after the end of the product's service life with the subsequent biodegradation of the obtained material fragments. The combination of a natural filler and a pro-oxidant additive in polymer compositions makes it possible to obtain a material with a programmed life and destruction.

Increasing population growth and improved quality of life lead to increased consumption and large amounts of waste.

Waste generation leads to loss of materials and energy, as well as additional economic and environmental costs for society in connection with the collection, recycling and disposal of waste. The impact of waste on the environment, resources and human health depends on their quantity and nature. Environmental pressures from waste generation and handling include emissions to air, water and soil, which have potential effects on human health. Most of the municipal waste is landfilled. It is necessary to take into account the fact that the volume of household waste increases annually, and territorial opportunities decrease, which leads to a negative impact on the environment. However, only a small part of the waste is recycled.

Over the past several decades, the formation of urban waste has increased dramatically. On average, the per capita amount of waste is 150–300 kg/year, and the annual increase in the amount of garbage is at least 3%, and in some countries, about 10% [1].

Waste can be domestic, industrial and mining. According to the phase state, they are divided into liquid, solid, or a mixture of solid, liquid, and gas phases (the emission of gases into the atmosphere through pipes is considered to be production emission, not waste).

Municipal solid waste (MSW) - waste generated in residential and non-residential premises in the process of consumption by individuals and legal entities, as well as goods that have lost their consumer properties in the process of consumption by individuals or legal entities in order to meet personal and domestic needs [2].

Solid municipal waste is very diverse in composition: food residues, paper, scrap metal, rubber, glass, wood, cloth, synthetic substances. The morphological and granulometric composition of MSW depends on the source of education and economic conditions, the population of cities, as well as the climatic conditions of populated areas.

According to numerous sources [3,4], 90% of MSW can be used to obtain secondary raw materials or additives to fuel resources. According to data published by Rosprirodnadzor, 9 million tons of waste paper, 1.5 million tons of ferrous and non-ferrous metals, 2 million tons of polymeric materials, 20 million tons of food waste and more than 0.5 million tons of glass are lost each year when disposing of unsorted MSW [5].

In Russia over the past 25 years, household waste has become 4 times more. This happened also because of the improvement of packaging culture (paper and cardboard, containers made of glass, as well as of complex composite materials) and the appearance of a large amount of disposable packaging (polyethylene film, polyethylene terephthalate, polyurethane foam, and other polymers).
Comparing the results of the morphological composition determining of municipal waste in Moscow in 2015 with the results of a similar study in 2008, showed an increase in the proportion of polymers and a decrease in the amount of glass waste is observed [6]. This is due to the decision of some food manufacturers to replace the glass packaging on the polymer, as cheaper. It is predicted that by 2025 the volume of polymer waste in Russia will amount to 7 million tons [7].

At the turn of the XX - XXI centuries for Europe, the problem of recycling polymer packaging is in fourth place, second only to outdated cars, worn car tires and demolished building waste [8].

Degradation of plastic waste by various methods (such as biodegradation, compost, oxo-biodegradation and photodegradation) becomes an alternative to solving such problems [9]. As a result of extensive research in this area, several basic strategies have been developed to solve the problem of pollution caused by polyethylene film [10]. First, the introduction of natural biodegradable fillers into the polymer matrix, secondly, the introduction of carbonyl groups directly into the polyethylene chain or into the α-position of short branches by copolymerization, and third, the introduction of a small amount of prooxidants [11]. Undoubtedly, the latter is more economically feasible, since in this case the existing production and processing technologies remain. It should be noted that in most cases a controlled service life is required from polymeric materials before physical degradation occurs; which implies the preservation of operational properties (physico-chemical and mechanical characteristics) of the product during the entire period of storage and operation [12].

Traditionally, natural fillers such as cellulose, starch, chitin, wood flour, etc. are used as additives to accelerate the biodegradation of polymer composite materials. Such natural fillers act as a nutrient medium for microorganisms, thereby increasing the contact surface of bacteria / micromycetes with polyolefins (not only from the surface, but from the volume) [13].

In the last decade, pro-oxidant additives have proven themselves well as additives to polyolefins [14]. Their composition usually includes stearates or carboxylates of metals with transition valency. They act as catalysts for the oxidation processes of (thermo-, photo-) polymers, which leads to preliminary breaking of the polymer chain, the accumulation of oxygen-containing groups and fragmentation of the material with subsequent biodegradation. According to ASTM D-5488-94d, biodegradation is defined as “the process by which materials are decomposed into carbon dioxide, methane, water, inorganic compounds or biomass, and the main mechanism is the enzymatic action of microorganisms.”

It should be noted that at the moment there are a large number of works aimed at:

1. study of the influence of various types of natural fillers and their content on the structure and properties of composite materials;
2. selection of pro-oxidants for polyolefins. However, due attention has not been paid to the creation of new composite materials polyolefin / natural filler / pro-oxidant additive and the study of the process of their biodegradation.

Oxo-biodegradable materials imply a two-step process of material degradation. At the first stage, oxo-decomposition of the material occurs, and at the second stage, biodegradation of fragments obtained as a result of oxo-decomposition. The aim of this work is to study the effect on the biodegradation of polyethylene with a natural filler of the introduction of the third component - a pro-oxidant additive and after preoxidized in air.

As the object of study, films of composite materials (table 1) based on low density polyethylene (LDPE) grade 15803-020 were used. The natural filler is cellulose of the Polycel PC brand (average fiber length 100 nm). A pro-oxidant additive that includes LDPE and metal salts of variable valency (cobalt, zinc and zirconium).
Table 1. Composite materials.

| №  | LDPE  | Cellulose | pro-oxidant additive |
|----|-------|-----------|----------------------|
| 1  | 70    | 30        | 0                    |
| 2  | 97    | 0         | 3                    |
| 3  | 67.9  | 29.1      | 3                    |

The stability of the studied films was determined in the soil, which was made in accordance with GOST 9,060-75. The essence of the method is to determine the change in mass of the samples after exposure for a certain time in a model environment. Soil parameters: humidity 30%, pH 7-8.

All samples were preoxidized in air at 90 °C for two days. For comparison, the results of the original samples.

Spectrometric studies were carried out using the equipment of the CCU “New Materials and Technologies” of the Institute of Bioorganic Chemistry, Russian Academy of Sciences, Perkin Elmer Spectrum 100, at T = 23 ± 2 °C in transmitted light in the wavelength range of 4600 – 450 cm⁻¹.

In the course of determining the stability of film samples in soil, the kinetics of mass loss was measured; the data are presented in Figure 1 for the starting materials (a) and after preliminary oxidation (b).

Figure 1. Kinetic curves of mass loss of samples 1 - PE / cellulose, 2 - PE / Cellulose / pro-oxidant additive (a) starting materials, (b) pre-oxidized.

It was previously shown that the introduction of a natural cellulose additive into the polymer matrix accelerates the biodegradation process [15]. But it should be noted that, preliminary acidification of the PE / cellulose composite material does not significantly accelerate the rate of weight loss. The introduction of a pro-oxidant additive in a potentially biodegradable material does not significantly increase weight loss. A preliminary oxidation of the composite material polyethylene / cellulose / prooxidant additive before entering the soil leads to rapid fragmentation of the material (Fig. 1b, curve 2) already in the second month of exposure.

Transition metals act as good prooxidants in polyolefins, so it makes the polymer susceptible to oxidative degradation. Transition metals induce hydroperoxide decomposition and produce free radicals on the polymer chain, which can attack chains and produce low molecular weight products with oxygen-containing groups, such as -COOH, -OH and >C=O groups[16,17]. While antioxidants and UV stabilizers make polyolefins resistant to degradation, prooxidant additives can make them oxo-degradable by catalytic chain breakage and make the polymer more hydrophilic. That is, oxo-
biodegradation means a two-step process, including, in order, oxidative destruction, which is usually abiotic, and then the biodegradation of oxidation products [18].

The literature reports that it is possible to achieve various rates of degradation by selecting a balanced combination of antioxidant and pro-oxidant additives [19, 20]. And by selecting a complex of salts of various metals in a pro-oxidant additive, you can control which environmental factor “triggers” the oxidation process to accelerate the subsequent biodegradation of the entire composite material. For example, Fe$^{3+}$ plays an important role in photooxidation, initiating a radical reaction [9]. Mn$^{2+}$ or Co$^{2+}$ are important oxidizing agents that initiate the decomposition of a polymer buried in soil in the absence of light.

In our case, the pro-oxidant additive contains: cobalt, zinc and zirconium, which have a good effect on the biodegradation of the material after preliminary oxidation with atmospheric oxygen, the material is phagmenated after a month of exposure.

It is known that during thermal oxidative degradation, the formation of free radicals O· and -OH occurs first, which turn into thermal decomposition products - ketones, esters, lactones and carboxylic acids [21].

For all samples, after exposure to the soil, changes in the region of 1800-1500 cm$^{-1}$ are recorded (Figure 2), which characterizes the formation of oxygen-containing products of thermal oxidation of polymers.

![Figure 2. IR absorption spectra of samples as a result of aging in soil, where 1 is PE / cellulose, 2 is PE / Cellulose / pro-oxidant additive (a) starting materials, (b) pre-oxidized.](image-url)
The absorption spectra for PE / cellulose samples, both for non-oxidized (Figure 2, 1a) and oxidized samples (Figure 2, 2a), have bands of 1715 cm⁻¹ — carboxyl groups and 1647 cm⁻¹ — terminal vinyl groups [22].

In the absorption spectra of PE / cellulose / pro-oxidant additive samples, intense absorption is recorded in the band region 1715 cm⁻¹, 1780 cm⁻¹ - aldehyde groups, 1740 cm⁻¹ - ketone groups, and absorption in the region 1650 cm⁻¹ - 1530 cm⁻¹ - amide I and amide II [22].

In addition to the main difference in the increase in the number of unsaturated oxygen-containing groups in the images containing the pro-oxidant additive, it is necessary to note the presence of absorption characteristic of amide I and amide II. This may indicate the growth and development of micromycetes and soil bacteria in the bulk of the material, i.e. about their penetration into the material and the course of biodegradation processes in the polymer matrix of composites.

The process of biodegradation of polymeric materials or their compositions in nature is not possible to consider in terms of only one factor causing degradation. Traditionally, the biodegradability of prooxidant activated polyolefins has been evaluated in complex media such as soil, sewage sludge or compost. This approach brings several advantages, such as the availability of a very diverse microbial inoculum or a close relationship to actual conditions in nature and / or in waste treatment processes.

Understanding the whole complex of the reactions is of great importance for researchers and technologists when creating biodegradable polymeric materials. Thus, the combination of a natural filler and a pro-oxidant additive in polymer compositions makes it possible to obtain a material with a programmed life and destruction. The introduction of a pro-oxidant can significantly accelerate the biodegradation processes (up to several months in the soil) with final fragmentation of the sample under the condition of preliminary acidification in order to form unsaturated oxygen-containing groups.

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