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## THE OXIDATIVE AND BIOLOGICAL DESTRUCTION OF COMPOSITE MATERIALS BASED ON LOW-DENSITY POLYETHYLENE AND LIGNOCELLULOSIC FILLERS

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**Abstract.** In this work 20 new biodegradable materials from polyethylene and lignocellulosic fillers were examined. The samples with and without compatibilizer were compared. This work contains four different methods of investigation: TGA, microscopy, thermal oxidation, biodegradation in soil.

**Keywords:** banana skin, biodegradable polymer, lignocellulosic filler, polyethylene, sodium lignosulfonate, sunflower husk.

### 1. Introduction

Synthetic polymer materials were first synthesized industrially relatively recently, in the middle of last century. They are widely used as constructional, insulating, building, packaging and other materials. World production of thermoplastic polymers in 2010 was about 245 million tons per year. The most popular polymers are polyethylene (38 % of consumption) and polypropylene (14 %). These materials are commonly used in various industries. Packaging accounts for 40 % of all thermoplastics, building materials up to 25 %, 10 % for motor-car construction and 8 % for electrical engineering. Thus, the most large-capacity polymer in Russia is polyethylene, which is used mainly for packaging. [1]

The access cycle of polymeric packaging materials is not long, so in short time after their production these materials are usually disposed of in landfill sites. Synthetic polymers do not decompose under natural conditions because of their chemical structure, and this is harmful for the environment. The evidence of this trend is the rate of plastic waste accumulation in landfills – 3.3 million tons per year, and the overall production of

polymers – 4 million tons per year! Polyolefins are the most resistant to biodegradation. Thus, the task of creating a biodegradable polymer material, which would have all the useful properties of polyolefins and with a comparable price, is important.

There are two approaches for creating biodegradable polymer materials. The first approach involves the synthesis of new polymer materials, which would have the ability to decompose in the environment under the influence of moisture, ultraviolet radiation, oxygen, air and soil microorganisms. Such materials do not currently have all the useful properties of traditional polymers, and their price is much higher. The second approach involves the creation of composite materials from the traditional synthetic polymers and biodegradable fillers. Most of these materials have a common problem, the adhesion of the polymer matrix to the filler being poor. Because of this poor adhesion, the physical and mechanical properties of the material are reduced, and only the filler undergoes biodegradation. In order to improve the adhesion of the synthetic polymer matrix to the organic filler a third component is used, which acts as a binder (compatibilizer). We'll consider a number of double and triple composites of different mixtures in this paper.

### 2. Experimental

#### 2.1. Starting Materials

Low-density polyethylene (LDPE) of 15803-020 grade, manufactured by JSC "NefteHimSevilen" (Kazan, Russia) was used as the polymer matrix. The choice of the polymer was researched thoroughly. From many available

grades of polyethylene it was necessary to choose the one that would meet the following requirements: 1) suitable for contact with food; 2) the structure of macrochains is optimal for introducing the filler; 3) the melt flow rate is sufficiently high; 4) deeply researched and documented.

LDPE 15803-020 satisfies all these requirements.

When choosing a filler, a number of requirements were taken into account:

- 1) Rapid biodegradation in the environment.
- 2) Low price.
- 3) Environmentally friendly.
- 4) The temperature of thermal decomposition is above 433 K.
- 5) Easily shredding.
- 6) High water absorption.

A number of fillers, presented in Table 1, were selected, which met all the requirements.

Table 1

The choice of the fillers

Filler	The argumentation of the choice
Flax sheave (FS)	Withdrawal in the production of flax fibers
Sunflower husk (SH)	Withdrawal in the production of vegetable oil
Sodium lignosulfonate (LS)	Withdrawal in the production of cellulose and paper
Banana skin (BS)	Withdrawal of food production
Fallen leaves (FL)	Natural pollutant in cities
Straw (ST)	Agricultural waste

The low level of lignocellulosic filler adhesion with the polymer matrix is mentioned in a number of papers on related subjects [2-6]. The third component, linking the polymer matrix and the filler, should be added to the mixture in order to improve the adhesion. Usually used for this purpose are so-called compatibilizers – substances based on polymers with an inoculated functional group. The most common compatibilizer used abroad is maleic polyethylene (polypropylene), available at a number of companies under the trademarks Polybond and Fusabond.

In this paper, we used a polymer with a similar structure, which is commercially produced in Russia under the trademark Sevilen (EVA). EVA is a copolymer of ethylene with vinyl acetate. The different contents of vinyl acetate may be added into the copolymer, defining the type of EVA. In this paper, EVA was used with an average content of vinyl acetate, the grade 11607-040 of JSC "NefteHimSevilen", Kazan. It was shown in a number of studies [6-9] that the content of the filler in the composition must be less than 30 % for making films. The content of compatibilizer should be 5–15 % of

polyethylene. In addition, the hydrogel (polyacrylonitrile) was added into two compositions. There was an idea to accumulate the moisture from the environment into a hydrogel for the rapid degradation of the samples, using microorganisms as well as the influence of the physical increase of the hydrogel particles in a polymer matrix. As a result, a few groups of samples were made, presented in Table 2.

Table 2

The composition of the samples

No.	Filler, mas %	LDPE, mas %	EVA, mas %	Hydrogel, mas %
1	FS, 30	70	-	-
2	FS, 30	66.5	3.5	-
3	FS, 30	59.5	10.5	-
4	FS, 30	49.5	10.5	10
5	SH, 30	70	-	-
6	SH, 30	66.5	3.5	-
7	SH, 30	59.5	10.5	-
8	LS, 30	70	-	-
9	LS, 30	66.5	3.5	-
10	LS, 30	59.5	10.5	-
11	LS, 30	49.5	10.5	10
12	BS, 30	70	-	-
13	BS, 30	66.5	3.5	-
14	BS, 30	59.5	10.5	-
15	FL, 30	70	-	-
16	FL, 30	66.5	3.5	-
17	FL, 30	59.5	10.5	-
18	ST, 30	70	-	-
19	ST, 30	66.5	3.5	-
20	ST, 30	59.5	10.5	-
21	-	100	-	-

The components were mixed with the roll mills at the temperature of 433 and 413 K.

This method of mixing provides an even distribution of the filler into the polymer matrix. After cooling, the pieces of material produced were shredded using an RM 120 cutting mill. Shredded material was pressed using a hand operated hydraulic press PRG10, with an electronic block for heating plates. The samples were pressed at a temperature of 413 K under the pressure of 7 kN for 3 min. As a result, the film samples obtained were round with the diameter of 7 cm and the thickness of 80 to 150 microns, depending on the filler.

## 2.2. Investigation Methods

The samples were exposed to a number of tests in order to determine their structure and properties.

The temperature of thermal degradation is an important criterion for the selection of the filler because the process of creating a composite material includes a mixture of the filler with the polymer at the processing

temperature of the polymer. Thermogravimetric analysis using a vacuum-tight micro-thermobalance NETZSCH TG 209 F1 was made for studying the degradation temperature of the fillers.

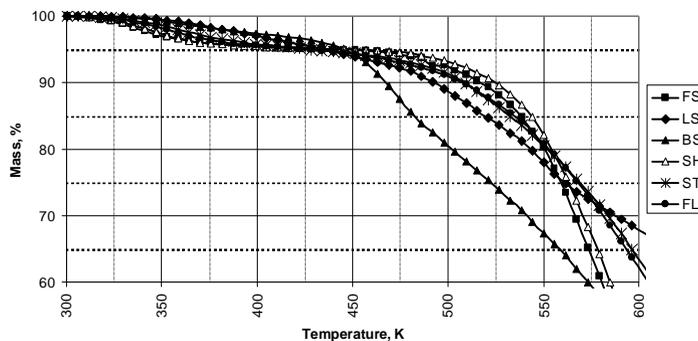


Fig. 1. The data obtained from a thermogravimetric analysis of different fillers

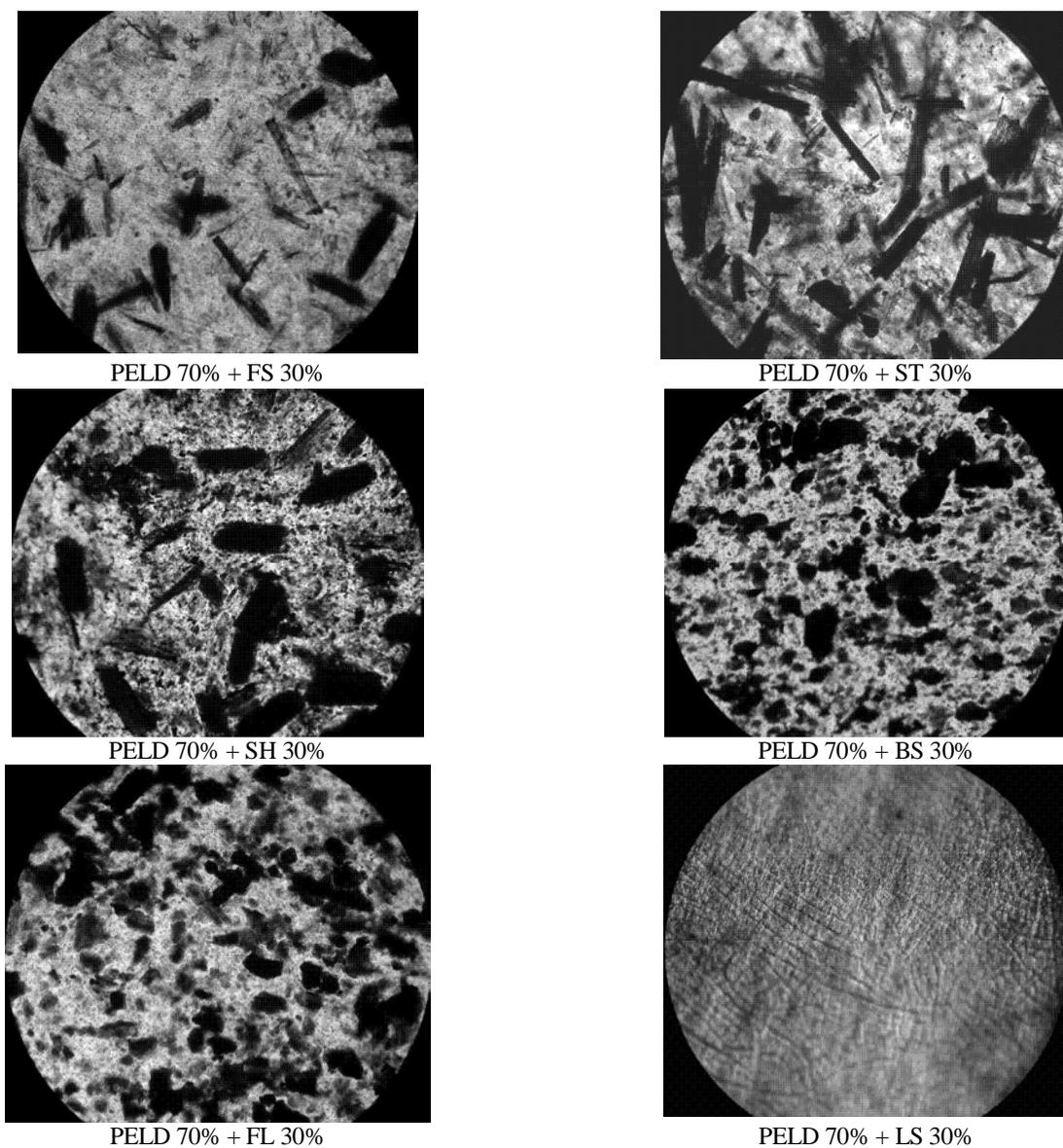


Fig. 2. Photomicrographs of different samples; magnification of 100x

One of the main methods for studying the structure of the composite materials is *optical microscopy*. As we used 6 different fillers, it was important to determine the size and form of the particles, the equitability of filler's particles in a polymer matrix and the relationship of size and form of the particles with other characteristics of the material. The photomicrographs of the samples were made using an optical microscope Olympus CX41 in transmitting light at hundredfold increase.

The laboratory method of the *thermal oxidation* models the destructive process that occurs under natural conditions over many years. The samples were placed in test tubes, and the oxygen was fed under pressure. The tubes were placed in a thermostat and heated to the required temperature.

One of the biggest challenges in the study of biodegradable polymer materials is the choice of methods to estimate the biodegradability of the materials. The best known methods are the following: "Sturm" – sturm test (OCDE 301B, ISO 14852) for 180 days (OCDE 301B, ISO 14 852), "Compost" – compost test under laboratory conditions (ISO/DIS 20200, EN 261085, ISO 14855) for 50 days, "Soil test" – test on reconstructed soil in the laboratory (DIN 53739) for 84 days, "Agricultural soil test" – sample is buried in real agricultural soil for 330 days, "Enzyme test" [8].

### 3. Results and Discussion

#### 3.1. TGA

The majority of the fillers do not undergo thermal destruction at temperatures below 493 K. The only filler, which stands out by this index is the banana skin, which has a destruction temperature of 438–448 K. The melt temperature should be 433 K for the optimum mixing of the filler with the polyethylene, and the temperature of destruction of the components should be 20 degrees above. Thus, all the selected fillers, except for a banana skin, are suitable for producing composites at the temperature of 433 K. For the compositions with a banana skin, the optimal temperature is 413 K. The temperature of LDPE destruction is  $513 \pm 5$  K.

#### 3.2. Microscopy

The photomicrographs of the samples are represented in Fig. 2. All the fillers used were sifted through a sieve with a mesh size of 200  $\mu\text{m}$ , to standardize their size. However, the form of the particles is different; for instance flax sheave and straw have a similar particle form of long fiber fragments, whereas fallen leaves and banana skin have a spherical particle

form. The particles of lignosulfonate are so finely dispersed that they are not even distinguishable in the microscope at a given resolution. It is obvious that this factor influences the difference in properties of the materials.

#### 3.3. Thermal Oxidation

The kinetics of the oxygen absorption was fixed, within certain time intervals. A graph of the kinetic curves of oxidation is based on these results. As a result, it is possible to define the role of every filler in the process of oxidation. Oxidation of polymeric materials is one of the processes occurring in the environment, which contributes to biodegradation of the samples. Thus, with the data obtained, we can indirectly define the biodegradability of the materials. For a full examination of biodegradation it is also required to consider the effect of water absorption and soil microorganisms. The melting point of polyethylene is 378 K, according to the DSC. The optimum temperature below the melting peak is 363 K, because the rate of chemical reactions is high enough, but the amplitude of the vibrations of atoms and molecules doesn't reach a critical value determined by the distance between neighboring molecules, so there is no melting of crystalline regions. The experiment was performed in a static manometric installation with the absorption of products of the reaction by solid KOH.

The material from the husk oxidizes most rapidly. This is explained by the presence of vegetable oils with unsaturated hydrocarbon chains, which readily react with oxygen (Fig. 3). The influence of different fillers on the kinetics of oxidation is obvious. Some fillers (SH, FS, ST, FL) accelerates the process, while others (LS and BS) inhibit it. The oxidability of fillers is not directly related to the compositions oxidation. For example, the sheave itself is oxidized less intensely among other fillers, but its compositions are the leaders in this index. When comparing samples of binary and ternary mixtures, it is obvious that the addition of EVA accelerates the oxidation (Fig. 4).

#### 3.4. Biodegradation in Soil

Fungi are the best destructors among the multitude of organisms that make a destructive effect on the materials. However, apart from fungi, the polymers can also be destroyed by bacteria, insects and rodents [9]. All of these factors have a complex effect on the material when it is buried into the ground, so the most suitable method for studying complex biological degradation is a test on reconstructed soil. Reconstructed soil models the real conditions of landfill sites, as it levels out the difference between soil types, ensuring high

reproducibility. The most suitable Russian standard, describing the decomposition of polymer materials in the soil is "Fabrics. Laboratory test for resistance to microbial decomposition". The soil has been prepared in accordance with this standard; the humidity was maintained at  $60 \pm 5\%$ . The test provides burying the film samples vertically into the ground, exposure for a certain period of time and then weighing the samples. The experimental results on the biodegradation in soil are presented in Fig. 5, where the numbers correspond to samples shown in Table 2.

The addition of EVA and the hydrogel into composites accelerates the biodegradation. This is explained by increased water absorption of the material, giving better (relative to low-density polyethylene) biodegradability of EVA. In addition, the adhesion of the polymer matrix with EVA to the filler is better, and because of this the mass of the composite decreases not only by breaking down the filler, but also because of degradation of the associated polymer.

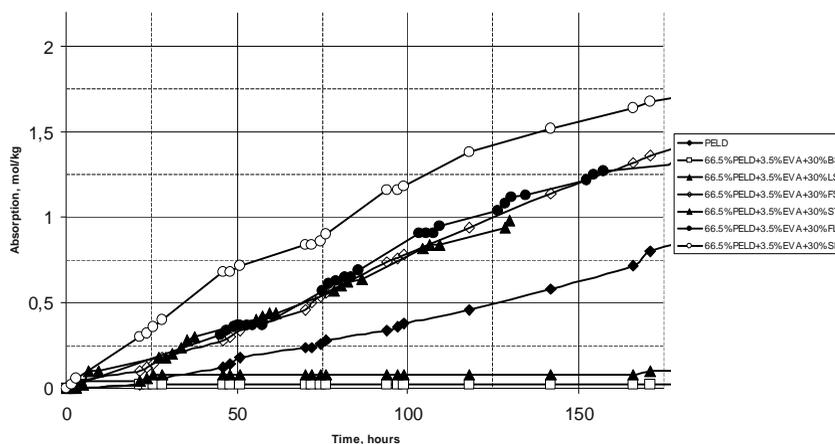


Fig. 3. The oxidation of composite materials with the temperature of 363 K

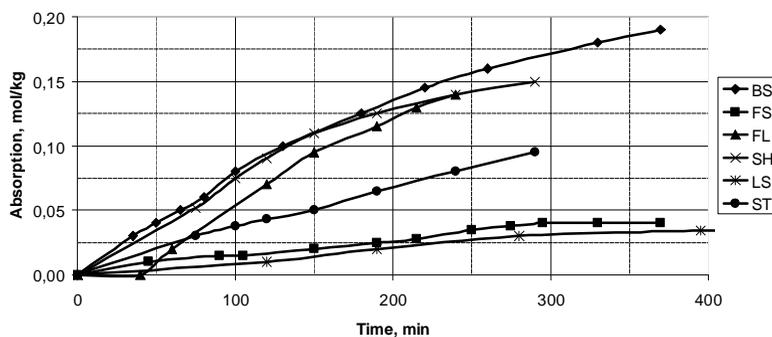


Fig. 4. The oxidation of the fillers with the temperature of 403 K

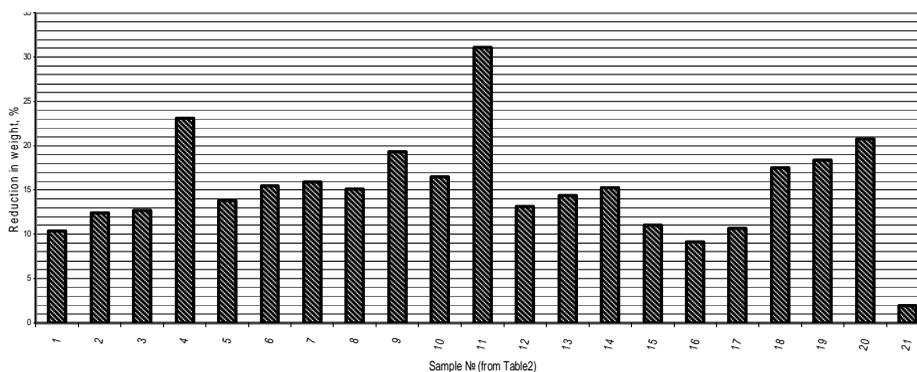


Fig. 5. The reduction in weight of the samples in soil

## 4. Conclusions

The results obtained in this work allow us to define the different properties of 20 new materials. Based on the properties of each material, it is possible to find their application. First of all, they may be used as film or bulk materials for packaging, such as bags, films, boxes, cushioning materials, transport pallets, etc. In addition, it is possible to produce different billboards, plates and other items that are usually made of plastic or cardboard, with the short access cycle from these materials. According to the results of the investigations presented here, the authors filed a patent application. The ability of using these materials for food packaging is researching now, according to primary data, it is possible for dry bulk products. The period of biodegradation of these materials depends on the type, shape and size of the manufactured article and the composting conditions, but anyway, it is about 2-5 years, that is ten times less than the period of degradation of the ordinary synthetic polymers.

## References

- [1] Kim S.: Rus. Chem. J., 2010, **8**, 54.  
 [2] Sivan A.: Current Opinion in Biotechn., 2011, **22**, 422.  
 [3] Lukanina Y.: PhD thesis, IBCP RAS, Moskwa 2011.  
 [4] Bledzki A. and Faruk O.: Appl. Composite Mat., 2003, **10**, 365.  
 [5] Yang H-S., Gardner D. and Kim H-J.: J. Thermal Analysis and Calorimetry, 2009, **98**, 553.  
 [6] Tajvidi M. and Takemura A.: J. Polymers and Environ., 2010, **18**, 500.  
 [7] Shlyapnikov Y., Kiryshkin S. and Maryin A.: Antiokislitel'naya Stabilizatsiya Polimerov. Khimiya, Moskwa 1986.  
 [8] Feuilloley P., Cesar G., Benguigui L. et al.: J. Polymers and the Environ., 2005, **13**, 349.  
 [9] Pekhtasheva E.: Biopovrezhdeniya i Zashita Neproduvol'stvennyh Tovarov. Masterstvo, Moskwa 2002.

### ОКСИДАЦІЙНА ТА БІОЛОГІЧНА ДЕСТРУКЦІЯ КОМПЗИТНИХ МАТЕРІАЛІВ НА ОСНОВІ ПОЛІЕТИЛЕНУ НИЗЬКОЇ ГУСТИНИ ТА ЛІГНОЦЕЛЮЛОЗНИХ НАПОВНЮВАЧІВ

*Анотація.* Досліджено 20 нових біодеградабельних матеріалів на основі поліетилену та лігноцелюлозних наповнювачів. Проведено порівняння зразків з комтабілізаторами та без них використовуючи різні методи досліджень: ТГА, мікроскопічні дослідження, термічне окиснення, біодеградацію в ґрунті.

*Ключові слова:* бананова шкіра, біодеградабельний полімер, лігноцелюлозний наповнювач, поліетилен, лігносульфат натрію, насіння соняшника.