

Biological degradation of gas-filled composite materials on the base of polyethylene

E A Grigoreva^{1,4}, N N Kolesnikova¹, A A Popov^{1,2} and A A Olkhov^{1,2,3}

¹ Emanuel Institute of Biochemical Physics of Russian Academy of Sciences, Kosygina st. 4, Moscow, 119334, Russia,

² Plekhanov Russian University of Economics, Stremyanny per. 36, Moscow, 117997, Russia

³ Semenov Institute of Chemical Physics of Russian Academy of Sciences, Kosygina st. 4, Moscow, 119991, Russia

E-mail: aquamirabilis@yandex.ru

Abstract. Gas-filled composite materials based on polyethylene were obtained. It was assumed that introduction of porosity in polyethylene will improve the biodegradability of synthetic materials. The morphological and structural changes were estimated, physical and mechanical properties, stability in water and soil of these materials were determined. It is stated that filling the polymer matrix with pores increases the ability to degrade in nature.

1. Introduction

Polyethylene comes forward in capacities of production and consumption in comparison with all other kinds of polymers in Russia. It is resistant to chemical and biological factors, meets high operational requirements. But after use it stays the same in landfills for hundreds of years, emitting harmful substances. The problem to improve the ability of polyethylene and other industrial synthetic polymeric materials (polypropylene, polyvinylchloride, polystyrene, polyethylene terephthalate) to degrade in natural conditions takes an important place among scientific researches [1, 2].

One of the ways to solve this problem is to make compounds of synthetic polymers with biodegradable components that are able to initiate fragmentation of a material or even decay of a polymer chain. Scientists develop this trend by making different kinds of composite materials, based on polymer matrix. Some researchers propose to add natural polymers [3-5]. Other scientists offer biocomposites containing finely divided particles of natural origin [6-8]. In some researches vegetable waste products are added to the polymer that helps to get not only biodegradable but inexpensive materials [7,9]. A synthetic matrix provides fine operational properties; an addition of natural filler provides a possibility to degrade after use. Structure, physical and mechanical properties, stability in water environment and soil of these compositions should be investigated [5].

The resistance of polymers to biological factors is due to the high degree of crystallinity and big sizes of molecules [10]. Addition of nature components makes the structure heterogeneous, decreasing resistance to different destructive factors. The process of filled polymer destruction starts with the natural component first, then the polymeric matrix declines. The polymeric framework, involved in



biological processes, decomposes in terms of oxidation and hydrolysis. These reactions cause fragmentation of the polymer because of macromolecules destruction and chain length reduction.

The aim of this work was to make gas-filled compositional materials, to investigate their structure and properties and reveal the influence of the porous structure on the ability to degrade in nature; then to choose compositions with optimal properties for adding natural component to it.

2. Experimental part

2.1. Objects and methods

The research considers compositions on the basis of low density polyethylene. A blowing agent - hydrocerol was added to make the structure porous. Wood flour with average particle size of 0.08, 0.14, 0.2 mm and starch with particle size 0.1 mm were added as natural disperse fillers.

Compositions of the polyethylene with hydrocerol were proposed (table 1). The hydrocerol contents were: 0, 1, 3, 5, 10 and 15wt%. Compositions were made by mechanical blending on the laboratory micro-rollers, warmed to 120°C. Then the compositions were foamed by using laboratory manual hydraulic press at 160°C (decomposition temperature for hydrocerol) without loading. Such a method allowed getting flat gas-filled plates.

Table 1. Compositions of test samples.

Number of the composition	Quantity of polyethylene (%)	Quantity of hydrocerol (%)
1	99	1
2	97	3
3	95	5
4	90	10
5	85	15

The density of samples was determined by the hydrostatic weighing method. Parameters of the structure were investigated by the optical microscope (Axio Imager Z2m Carl Zeiss, Germany). Thermophysical parameters (polyethylene melting temperature, gas formation temperature and the degree of crystallinity) were measured by differential scanning calorimetry on micro-calorimeter (DSM-10m, Russia). Listed above studies were carried out with the equipment of the Center of Shared Usage «New Material and Technologies of Emanuel Institute of Biochemical Physics». Water absorption was measured by samples weight change in distilled water. The ability to degrade in the environment was measured by samples weight change in soil.

2.2. Results and discussion

The thermogram of heating samples of polyethylene, polyethylene with hydrocerol is presented in figure 1. It shows two peaks that give an idea of temperatures of melting and gas formation. The first peak corresponds to the process of polyethylene melting (106°C). The second peak corresponds to the process of gas formation (160°C). It did not appear in case of pure polyethylene. With the help of the computer program «Peak Explorer» squares of peaks were determined and the degree of crystallinity was measured. The investigation of samples with the different content of hydrocerol showed that thermal effect of hydrocerol decomposition is directly proportional to its content in the polymeric mass. The degree of crystallinity stays almost the same (28%) in spite of hydrocerol containing change.

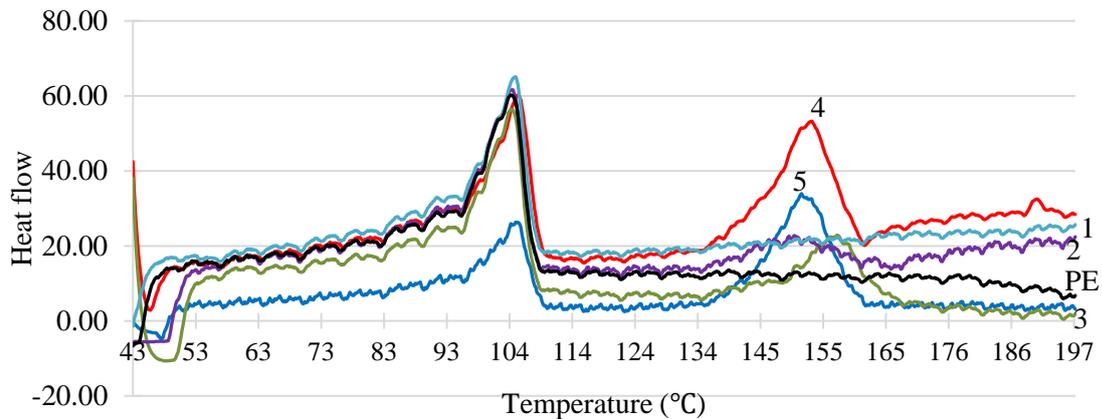


Figure 1. Thermograms of melting and gas formation: thermogram of heating samples of polyethylene (PE), polyethylene with 1% (1), 3% (2), 5% (3), 10% (4) and 15% (5) of hydrocerol.

At the next stage, the structure of samples was investigated. Microphotographs of the gas-filled samples in case of magnification 100x are shown in figure 2. The investigation of cross section of samples presents that pores appear in the polyethylene matrix. In samples with the low content of blowing agent pores and cells have clear regular spherical shape with smooth walls, isolated from each other and from the external environment. Within an increase of hydrocerol content a number of cells is growing, their shapes are getting irregular, walls between them are thinning and destroying. The cells interpenetrate into one another, connect with each other and with the external environment.

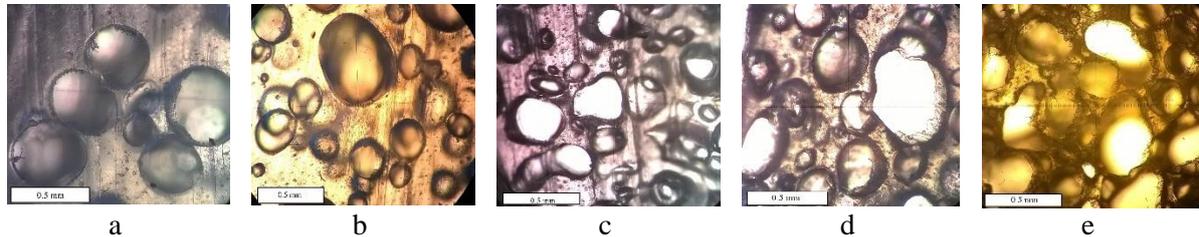


Figure 2. Microphotographs of the gas-filled samples of compositions with different hydrocerol content, a – 1%, b – 3%, c – 5%, d – 10%, e – 15%.

Diameter of pores and thickness of walls between it were measured, making the assumption, that all pores have a clear and spherical form. The average diameter of pores varies from 0.21 to 0.40 mm, few pores had bigger diameters (0.61-0.80 mm) and few pores had larger diameters (0 – 0.20 mm). The average thickness of walls of pores varies from 0.01 to 0.40 mm; walls with thickness of up to 0.10 mm prevail. The results of this measurement are given in figure 3, a - pores, b - walls. A number of pores per 1 mm² was calculated. It varies between from 9.6 to 12.5.

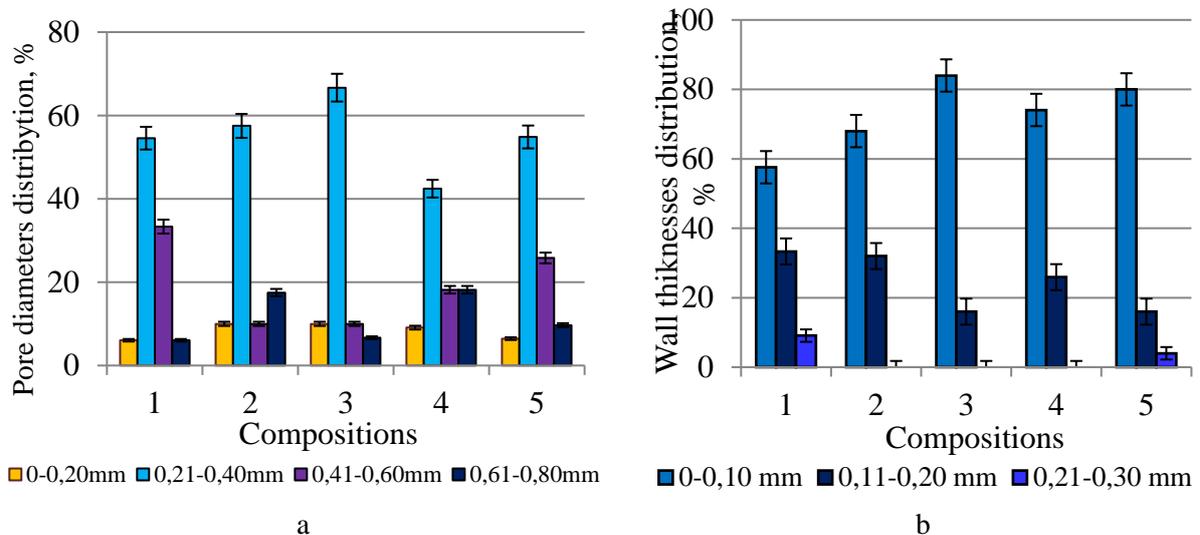


Figure 3. Size distribution of elements of the structure, a – cells and pores, b – walls.

The structure of the gas-filled materials corresponds to schemes given in figure 4. A scheme, pictured in figure 3a, is more likely to match gas-filled polyethylene with the hydrocerol content of 1 – 10%. This is a porous structure with closed, isolated cells. A scheme, pictured in figure 3b, is more likely to match samples with the hydrocerol content of 15%. These samples contain many connecting and interpenetrating cells.

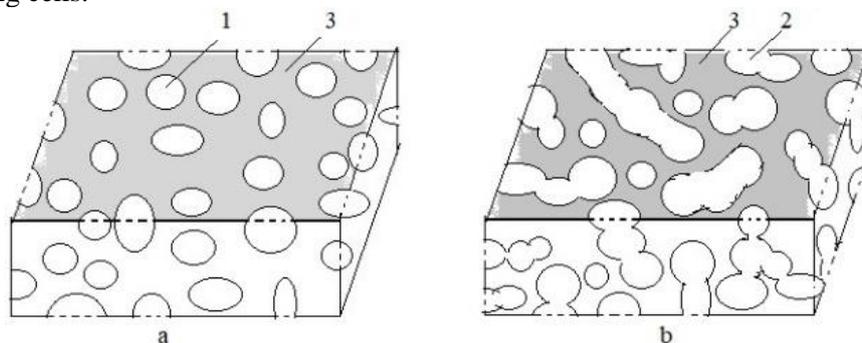


Figure 4. Types of the structure: a – with isolated cells, b – with interconnected cells; 1 – cell, 2 – pore, 3 – polymer.

Such factors as the number of cells per 1mm^2 , a type of the structure, a shape of cells are crucial for operational and consumer properties. On the one hand, gas-filled polymeric materials are valued for its low density, fine isolating properties [11]. On the other hand, these materials may be characterized by low strength properties. So, it is important, to determine density, tensile strength and elongation at break of the samples.

The density of test samples, depending on hydrocerol content, was determined and compared to the pure polyethylene (table 2). As seen from the table, the density of gas-filled materials is lower than the one of polyethylene. There is no direct correlation between the density and the composition of the samples. The sample with hydrocerol content of 10% has the lowest density (0.33 g/cm^3), but the sample with hydrocerol content of 15% shows an increase to 0.55 g/cm^3 . It may be explained by the fact that a solid residue accumulates during the reaction. It is known that only 40% of hydrocerol decomposes with emission of gas (CO_2) during gas-blowing. The other 60% of hydrocerol produces a solid residue.

Table 2. Density of test samples under investigation.

Hydrocerol content (%)	Density (g/cm ³)
0	0.92
1	0.58
3	0.73
5	0.57
10	0.33
15	0.55

Tensile strength and elongation at break of polyethylene (PE) and the test samples were investigated to learn mechanical and operational properties (table 3). As seen from the table, filling the structure with gas does not make much influence on the strength of polyethylene samples. Nevertheless, elongation at break decreased by about 10%. It may be due to forming thin walls of pores.

Table 3. Tensile strength and elongation at break of test samples.

Compositions	Tensile strength (MPa) ±0.5MPa	Elongation at break (%) ±2%
PE	10.0	74
1	9.7	65
2	9.5	64
3	9.4	67
4	9.1	63
5	9.1	65

Gas bubbles make the structure heterogeneous, cause formation of defects, which, in its turn, initiate formation of nascent pores, microscopic cracks. Such a structure is not equilibrium. It will be able to degrade faster into microscopic pieces under environmental conditions, namely microorganisms, oxygen, moisture, water, temperature changes and so on.

When gas-filled materials get to environmental conditions, moisture starts to penetrate in it through pores. And the moisture is the enabling environment for development of microorganisms. On this step the idea was to estimate how different hydrocerol contents influence water absorption. Main factors, influencing the speed of water absorption, are presented below:

- the chemical structure of a polymer and gas, namely permeability of this material for water;
- the size of cells or pores, which means that the large number of small cells exert stronger resistance to penetration of moisture than the little number of big cells;
- presence of open cells on the surface or compacted surface crust.

Results of investigating of water absorption of samples of polyethylene and gas-filled materials during eleven days are given in figure 5. As seen on the picture samples of polyethylene and material with hydrocerol content 1%, 3% absorb less water (not more than 4%). With an increase of hydrocerol content the structure becomes a system with a number of connecting and interpenetrating cells that leak and accumulate moisture.

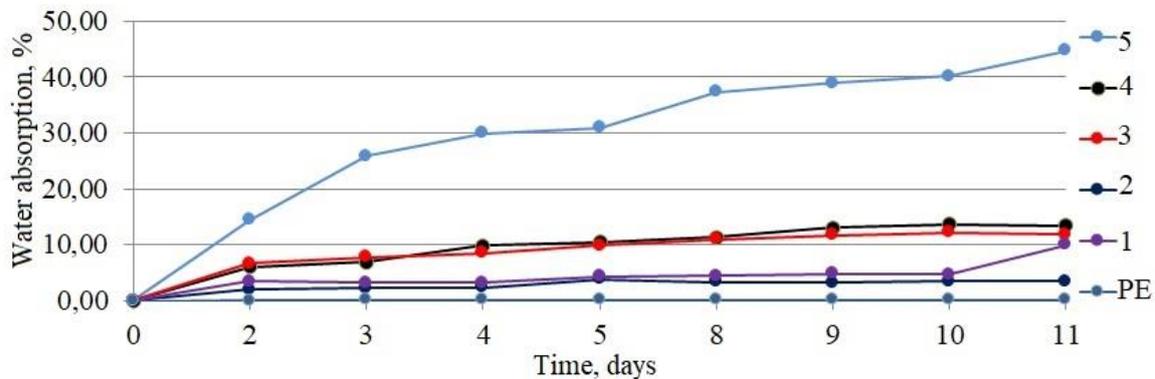


Figure 5. Water absorption of polyethylene and gas-filled samples during 11 days.

The samples were kept in soil to estimate the ability of the material to degrade in a landfill. The change in mass as compared with the initial mass was measured. Course of degradation was controlled by periodic weighing of the test samples. The samples were expected to demonstrate weight loss because of fragmentation. Results of investigating changes in mass of test samples during thirty six months are given on figure 6.

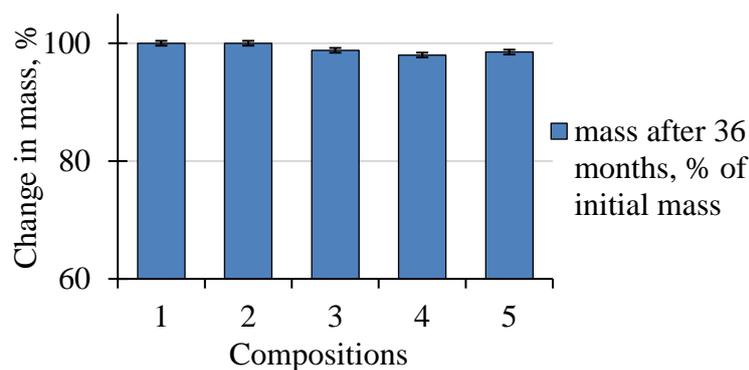


Figure 6. Changes in mass of gas-filled samples after 36 months in soil.

Addition of the finely divided particles of natural fillers is made to samples with initial hydrocerol content 5 and 15%. This will lead to accelerating processes of biological destruction of the materials. Microphotographs of several gas-filled composite samples with wood flour (WF) and starch in case of magnification 100x samples are given in figure 7.

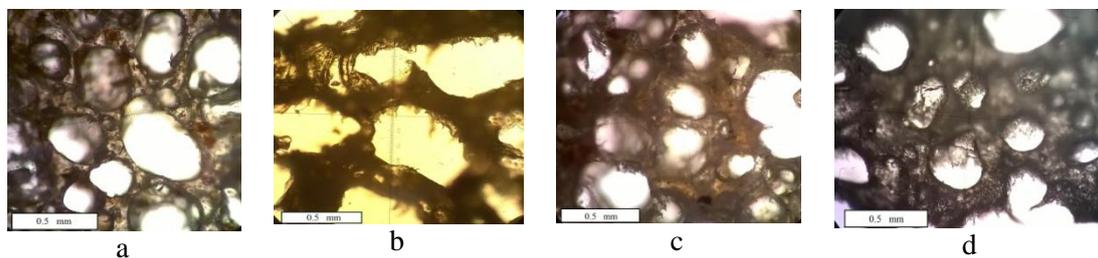


Figure 7. Microphotographs of the gas-filled compositions with addition of 15% of natural fillers, a – with 5% of hydrocerol, WF of 0.14 mm; b – with 5% of hydrocerol, WF of 0.20 mm; c – with 15% of hydrocerol, WF of 0.08 mm; d – with 15% of hydrocerol, starch.

The form of pores and cells was distorted when the particles were introduced. Addition of components, that are hygroscopic, swelling in water, leads to significant increase of water absorption.

Penetration of moisture, soil and microorganisms into the material is becoming easier. The particles can be washed out of the matrix by water or assimilated by microorganism.

Addition of fillers will lead to decrease of tensile strength because the structure would be more heterogeneous. It is suggested to produce goods for short-term use on the base of these compositions (packaging materials, packaging elements, elements of medical or cosmetology tools).

3. Conclusion

Addition of hydrocerol to polyethylene leads to creation of porous structure. It is stated, that as the content of hydrocerol in the composition increases, the number of cells and pores in the samples becomes bigger, the thickness of pore walls decreases. As a result, mechanical and operational properties decrease.

The presence of pores in the polymer matrix promotes the penetration of moisture and microorganisms into it. Such materials will decompose in landfills under the influence of physical, mechanical and biological factors.

Addition of a natural filler makes the structure of gas-filled material more heterogeneous and defective. Materials, containing wood flour or starch, will also destroy under the influence of biological factors. Thus, the presence of pores and natural filler particles in the matrix of synthetic polymer is vital for its biodegradability.

References

- [1] Arkatkar A, Arutchelvi J, Bhauri S, Uppara P V and Doble M 2009 *J. The Open Environ. Enj. J.* **2** 68-80
- [2] Harding K G, Gounden T and Pretorius S 2017 *J. Procedia Manuf.* **7** 106-110 doi:10.1016/j.promfg.2016.12.027
- [3] Rogovina S Z, Alexanyan C V and Prut E V 2011 *J. of App. Pol. Sc.* **121** 1850-59 doi:10.1002/app.33477
- [4] Olkhov A A, Tyubaeva P M, Staroverova O V, Mastalygina E E, Popov A A, Ischenko A A and Iordanskii A L 2016 *AIP Conf. Proc.* **1736** (US: AIP Publishing) doi: 10.1063/1.4949673
- [5] Mastalygina E E, Varyan I A, Kolesnikova N N and Popov A A 2016 *AIP Conf. Proc.* **1736** (US: AIP Publishing) doi: 10.1063/1.4949672
- [6] Mastalygina E E, Kolesnikova N N, Popov A A and Olkhov A A 2015 *AIP Conf. Proc.* **1683** (US: AIP Publishing) doi: 10.1063/1.4932833
- [7] Zykova A K, Pantyukhov P V, Kolesnikova N N and Monakhova T V 2017 *J. Polym. Environ.* doi: 10.1007/s10924-017-1039-9
- [8] Zykova A, Pantyukhov P and Popov A 2017 *J. Polym. Enj. And Scien.* doi: 10.1002/pen.24626
- [9] Pantyukhov P, Kolesnikova N and Popov A 2016 *J. Polym. Compos.* doi: 10.1002/pc.23315
- [10] Ashwin Kumar A, Karthick K and Arumugam K P 2011 *J. of Ghem. Enj. and App.* **2** 164-167
- [11] Toninski M 2015 *J. Additiv. for Polyolefins* 147-152 doi:10.1016/B978-0-323-35884-2.00013-2