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Research Article

The Effect of a Zinc-Containing Additive on the Properties of PVC Compounds

Irina N. Vikhareva (ID)**,**[1] **Guliya K. Aminova,**[1] **Alexander I. Moguchev,**[2]
and Aliya K. Mazitova (ID)[1]

[1]*Applied and Natural Sciences Department, Ufa State Petroleum Technological University, Mendeleeva St. 195, 450080 Ufa, Russia*
[2]*Department of Machinery and Equipment of Oil and Gas Fields, Ufa State Petroleum Technological University, Kosmonavtov St. 1, 450062 Ufa, Russia*

Correspondence should be addressed to Irina N. Vikhareva; irina.vikhareva2009@yandex.ru

Polymeric materials that undergo degradation under the influence of biological media have attracted widespread attention in recent decades. This is due to the ability to eliminate the negative impact on the environment, gradually reducing the scale of plastic waste pollution. At the same time, it remains relevant to ensure the necessary performance characteristics of products for a certain period of use. An important direction in the field of biodegradable composite compositions is the development of nontoxic additives in order to ensure their safe interaction with biological media. In this regard, a method has been developed for the joint production of a new nontoxic plasticizer decyl phenoxyethyl adipate and a biocidal additive of zinc decyl adipate. The effect of the obtained additives on the biodegradation of PVC film samples under natural conditions was studied. The period of biocidal action of zinc compound formed in situ in an amount of 0.3% in the composition of PVC films using the developed plasticizer was determined.

1. Introduction

For the first time, society faced a "solid waste crisis" in the 1980s. The high resistance of synthetic polymer materials to physical, chemical, and biological destruction contributed to an increase in the mass of household waste in burials near large cities [1]. In this regard, in the scientific literature, works have appeared on the creation of plastic degradable by microorganisms, that is, polymers with a chemical structure that is completely destroyed within an acceptable period of time (several weeks or months) when the material is exposed to microorganisms in soil and water [2]. In the developed composite materials, natural polymers were mainly used as raw materials.

However, the best solution is to create materials that would exist unchanged during storage and operation and then under the influence of certain factors (soil microorganisms, light, air oxygen, water, etc.) that would decompose within a short time.

Currently, existing biodegradable polymers, such as polylactides or polyhydroxyalkanoates, are more expensive than traditional polymers [3–5]. However, even with a decrease in their cost, synthetic polymers (polyolefins and polyvinyl chloride) in the near future will occupy leading positions in the production of plastics [6, 7].

Among polymers, polyvinyl chloride (PVC) ranks second in terms of consumption due to its high versatility and unique balance of low production costs [8]. Plasticized PVC is widely used in the production of various materials, such as medical devices, packaging, toys, artificial leather, and cable products. Therefore, one of the promising areas is the development of biodegradable polymeric materials based on PVC.

The possibility of obtaining cheaper biodegradable materials is mainly associated with the development of polymer compositions, including, along with traditional thermoplastic synthetic polymers, biodegradable additives or fillers of natural origin [9]. Among them are known biodegradable polymer compositions containing polysaccharides, starch,

cellulose, chitin, chitosan, and others as a filler [10–15]. However, some of the listed additives are valuable food products; therefore, the production of large-capacity materials on their basis for the manufacture of short-term products is economically unjustified. On the other hand, the use of such additives reduces the physical and mechanical characteristics of the materials obtained and, accordingly, degrades the quality of the products. Moreover, unlike commercial plastics, for example, polyolefins and PVC, such biopolymers are not amenable or poorly heat-treatable [16–19]. Disadvantages can also be attributed to the current technologies of their production, which consume a significant amount of energy and water and are characterized by emissions of pollutants into the environment [20–22].

Currently, there is a wide range of technological methods that allow to purposefully regulate the structure and properties of polymer composites due to the use of fillers and additives of various nature and fractional compositions [23–25].

Development and industrial production of new types of biodegradable plastics, the improvement of the performance characteristics of these materials, and the reduction of their cost contribute to a significant increase of interest in the [1]composting process and the methods of its implementation [26–31]. Recently, there has been a tendency to move from organized waste dumps with backfill to designed landfills for composting, as a result of which the growth and activity of the microorganisms used is achieved. Thus, the use of biodegradable plastics presents significant advantages if the final disposal of the waste stream is to be carried out by a composting process.

Almost all types of microorganisms, especially in conditions favorable for their growth, cause biodeterioration of polymer-containing materials [32–34]. Synthetic polymers and materials based on them are significantly superior in biostability to natural polymers (cellulose, collagen, etc.); however, under appropriate operating conditions, both species are damaged by biological agents, the main among which are microscopic fungi [35–38].

Some microorganisms, for example, filamentous fungi, are unable to immediately penetrate into the dense and porous structure of composite materials [33, 39]. However, in conditions of an ecologically contaminated environment, significant fouling by fungi of any polymeric material was noted. During the operation of plastics, biodamage caused by various microorganisms significantly degrades not only the commercial appearance but also the physical, mechanical, and technical characteristics of materials.

Creation of composites with the given bioavailability is carried out by the introduction of biocides into the material [40]. Among the general requirements for biocides are high efficiency of biocidal action, availability and relatively low cost, solubility in water, instability in natural conditions, ease of use, environmental safety, and low toxicity to humans [10]. The difficulty in choosing protective additives against biological damage is that the protective chemical agents themselves are not always neutral with respect to biocetonic and population communities [35]. Since polymer materials and products based on them are widely used in various areas of human life, special attention should be paid to the prevention of the toxicological consequences of the use of these protective means.

The first generation of biocidal additives contained tin, lead, mercury, and arsenic, which are considered highly toxic to warm-blooded animals and humans. Subsequently, many new biocides have been developed and used in commercial purposes to replace them [40–43]. Biocidal polymer additives are also widely used, for example, azolates, graphene, nanorods, and silver compounds [44–47]. Although some of them are biodegradable in a short period of time, less than 24 hours [43, 48, 49], they pose a threat to the environment, since they have a wide spectrum of action and affect nontarget organisms from low to higher trophic levels, especially in the first hours of activity, affecting the food chain [41, 50, 51]. In addition, the release process can be continuous, which contributes to long-term exposure.

The wider use of polymeric biocidal preparations is limited by insufficient knowledge of the relationship between their chemical structure and biological activity. For some of the polymer biocidal systems, the mechanism of action is still unclear [52–55].

Depending on the purpose and types of targets, biocides should have different properties. For use in some areas, water-soluble drugs that are distributed in a biological environment are more preferred.

Inorganic biocides, in particular, salts of transition metals, are one of the oldest groups of these additives, moreover, with the most well-studied mechanism of action. It is known that zinc compounds are not inferior in efficiency of biocidal action, but surpass the given examples in spectrum, acting on microorganisms not only as inhibitors but also as antimetabolites of enzyme systems, and are also more environmentally acceptable [56–58].

Due to their high biological activity, relatively low cost, and environmental safety, zinc compounds are very promising for use as biocidal additives, since they exhibit high antibacterial activity against a wide range of bacteria and fungi [11, 12, 59]. In addition, zinc compounds are biocides with a limited duration.

Therefore, due to the lack of a suitable replacement for traditional polymers, one of the promising directions is the development of composites based on them with the use of nontoxic additives that provide appropriate regulatory qualities for a certain period of operation and impart biodegradation to polymer composite materials.

Currently, in the processing of polyvinyl chloride, a wide range of additives are used that provide various functions during processing and operation. Due to the development of new processing methods and the use of high-performance equipment, multicomponent polyfunctional additives have begun to be actively used. The use of a mixture of correctly selected additives provides a synergistic effect and also allows you to significantly reduce the consumption of introduced components and, accordingly, the cost of production. In modern conditions, due to the accumulation of plastic waste, it is important to develop nontoxic additives that contribute to the preservation of technical and operational characteristics for a certain period and are capable of further degradation in environmental conditions.

Taking this into account, a new polyvinyl chloride ester plasticizer based on adipic acid ester was obtained for use in the PVC composition as a biodegradable additive. To catalyze the reaction, zinc oxide was used, from which zinc phenoxyethyl adipate was obtained in situ. Furthermore, comprehensive studies were carried out that aimed at studying the features of biodegradation of the developed polymer compositions.

2. Materials and Methods

2.1. Starting Materials. Adipic acid (Radici Group, Selbitz–Hochfranken, Bavaria, Germany) is a white crystalline substance with a main substance content of 99.8% and was used as received; it has a melting point (m.p.) of 153°C. Decyl alcohol (The Company «Rearus», Moskow, Russia) is a colorless transparent liquid that has a peculiar smell, with a main substance content of 99%, and is insoluble in water, soluble in alcohol, and other organic solvents with a boiling point (m.b.) of 231°C; it was used as received. Phenol ("Ufaorgsintez," Ufa, Russia) is a colorless needle-like crystal and was used as received; it has a melting point (m.p.) of 40.9°C. Ethylene oxide (ECOTECH Chemical Components Plant, Moscow, Russia) is a liquefied gas that is a colorless transparent liquid in steel cylinders with a boiling point (m.b.) of 10.7°C. Sodium hydroxide (Joint Stock Company "Caustic," Sterlitamak, Russia) is a white solid with a main substance content of 98.2% and was used as received. Zinc oxide (Component-Reagent, Moscow, Russia) is a colorless crystalline powder with a main substance content of 98%, is insoluble in water, and yellows when heated. Toluene (Public Joint-Stock Company "Joint-Stock Oil Company, Bashneft," Ufa, Russia) is a colorless liquid with a characteristic smell, and a main substance content of 99%, and was used as received; it has a boiling point (b.p.) of 110.6°C. Polyvinyl chloride (Joint Stock Company "Caustic," Sterlitamak, Russia): we used industrial samples of suspension polyvinyl chloride PVC 7059 M. The molecular weight was between 31000 and 94000. Suspension polyvinyl chloride made by suspension polymerization, with a K value from 70 to 73, with a bulk density from 0.45 to 0.55 g/cm^3, with a residue after sieving on a sieve with a mesh N 0063–95%, for the manufacture of plasticized products. It is a homogeneous white powder.

2.2. Synthesis Methods

2.2.1. Synthesis of Phenoxyethanol. A round-bottom flask equipped with a thermometer, a stirrer, a reflux condenser, and a device for introducing ethylene oxide into the reaction mass was charged with 94 g (1 mol) of phenol and a sodium hydroxide catalyst in an amount of 1.4 g (1% of the total mass of the reaction mixture).

The reactor was heated to 110–130°C and purged with nitrogen to remove air. Subsequently, 44 g (1 mol) of ethylene oxide was gradually introduced to the stirrer in operation. The ethylene oxide feed rate was adjusted so that the unreacted oxide condenses in the cooler and returns to the reactor without flooding. After feeding the entire amount of ethylene oxide, the temperature of the reaction mixture was

maintained for an additional 1–1.5 h and then cooled to room temperature.

The catalyst was neutralized with a calculated amount of sulfuric acid, and the obtained mass was filtered. The reaction mixture was then distilled off the fraction boiling to 50°C at 10 mm Hg.

Phenoxyethanol is a colorless oily liquid soluble in water. The yield was 122.8 g (89% of theoretical).

2.2.2. The Synthesis of Decyl Phenoxyethyl Adipate (DPEA). In a reactor equipped with a stirrer, thermometer, Dean-Stark attachment, 158 g (1 mol) of decanol was dissolved in 200ml of toluene; then, 3.0 g (1% by weight) of zinc oxide and 146 g (1 mol) of adipic acid were added, and the temperature was adjusted to 110 ± 10°C. Stirring was continued for 1.5 hours. The end of the reaction was determined by the amount of released water in the form of an azeotrope and the acid number of the reaction mass. When receiving a monoester of adipic acid, 1 mol of water is released per 1 mol of acid, that is, 18 g.

Then, without isolating the monoester, it was esterified with phenoxyethanol (138 g) taken in a molar ratio of monoester : alcohol = 1 : 0.93. The reflux was continued for 2 h, while the temperature was slowly raised to 130°C. The end of the reaction was determined by the amount of released water (0.93 mol, which is 16.74 g) and the acid number of the reaction mass. The reaction mixture was cooled, and the product was filtered and dried at 125°C. The yield of the light powder product was 363 g (89.5% of theoretical). The product was a mixture of decyl phenoxyethyl adipate (337.6 g) plasticizer and zinc decyl adipate stabilizer in an amount of 25.4 g.

Characteristics of the obtained products are presented hereinafter.

2.3. Methods of Analysis

2.3.1. Analysis of Physicochemical Parameters of Plasticizer. The analysis of physicochemical parameters of the obtained compound was carried out in accordance with state standard 8728-88 Plasticizer specifications [60]. For this, the following indicators were determined: Acid number, ester number, mass fraction of volatile substances.

Analysis of the acid number: the essence of the definition is the titration of an alcoholic solution of the test product with a solution of potassium hydroxide in the presence of a phenol red indicator. The acid number (X) in mg KOH/g is calculated by Formula (1):

$$X = \frac{V \cdot 5.61}{m}, \tag{1}$$

where V is the volume of 0.1 N sodium hydroxide solution used for titration of the sample, cm^3; 5.61 is the equivalent weight of potassium hydroxide; m is the sample weight taken for analysis, g.

The analysis of the ester number: the essence of the definition consists of titration with a solution of hydrochloric or sulfuric acid in the presence of phenolphthalein until the sample of a plasticizer and the solution of potassium hydroxide are discolored after heating for 1 h in a boiling water bath.

The ester number (X) in mg KOH/g is calculated by Formula (2):

$$X_1 = \frac{(V_1 - V_2) \cdot 56.1}{m}, \qquad (2)$$

where V_1 is the volume of a solution of hydrochloric or sulfuric acid with a concentration of 1 mol/dm³ (1 n), used for titration in a control experiment, cm³; V_2 is the volume of a solution of hydrochloric or sulfuric acid with a concentration of 1 mol/dm³ (1 n) spent on titration of a solution with an analyzed sample, cm³; 56.1 is the equivalent weight of potassium hydroxide; m is the sample weight taken for analysis, g.

Determination of plasticizer density was carried out according to state standard 18329–2014 "Liquid resins and plasticizers and methods for determination of density"[61].

2.3.2. Determination of Thermal Stability of Plasticizer.
Determination of thermal stability of plasticizer and polymeric compositions is based on polyvinyl chloride. To determine the thermal stability of the plasticizer and polymer compositions based on polyvinyl chloride, a TGA/DSC-1 thermal analysis device (Mettler Toledo, Greifensee, Switzerland) was used. Effects accompany the sample heating process. The temperature range of the device is 25–1100°C. The maximum volume of the test sample does not exceed 900 μL. The maximum heating rate of the sample is 150 K/min. The cooling rate of the device is 20 K/min. Measurement error is ±0.3 K.

The measurements of the thermal stability of the sample were carried out in the temperature range from 25 to 500°C in air. The measurements were carried out in a dynamic mode with a constant heating rate of 5 K/min. The mass of the sample used for measurements was 5–10 mg. For the analysis, we used alumina crucibles with a volume of 100 μL. The results were processed using a computer: STARe thermal analysis software.

When conducting research on the TGA-DSC-1 thermal analyzer, the following curves are recorded on the resulting thermogram of the sample, which were used to assess the thermal stability of the samples:

(i) Thermogravimetric curve (TG) characterizes the change in the sample mass during heating (the dependence of the mass on temperature)

(ii) The differential thermogravimetric curve DTG characterizes the rate of change in the sample mass during heating

(iii) the DSC curve characterizes the thermal effects observed during the heating of the sample

Determination of melting and crystallization temperatures of the plasticizer: the melting and crystallization points of plasticizer were determined by differential scanning calorimetry on a DSC-1 instrument. The temperature range of the device is from -150°C to 500°C. The sample is cooled with liquid nitrogen. The sample heating rate varies in the range from 0.02 to 300 K/min. The cooling rate of the device is from 0.02 to 50 K/min. Measurement error is ±0.2 K.

The measurements were carried out in the temperature range from -50 to 150°C in air. The measurements were carried out in a dynamic mode with a constant sample heating/cooling rate of 10 K/min. The mass of the sample used for measurements was 4–8 mg. For the analysis, aluminum crucibles with a volume of 40 μL were used. The weighed sample was placed in a crucible and sealed with a lid using a press.

The results were processed using a computer. Curves were displayed on the computer screen as a function of the change in the magnitude of the heat flux with temperature.

The melting point of the plasticizer was determined from the DSC curve obtained in the sample heating mode. The melting point of the plasticizer corresponds to the maximum value of the endothermic peak observed on the DSC curve.

The crystallization temperature of the plasticizer was determined according to the DSC curve obtained in the cooling mode of the sample after its preheating by 30-40°C higher than its melting point. The crystallization temperature of the plasticizer corresponds to the maximum value of the exothermic peak observed on the DSC curve.

Determination of the glass transition temperatures of PVC composition: the glass transition temperatures of PVC composites were determined by differential scanning calorimetry on a DSC-1 instrument (Mettler Toledo, Greifensee, Switzerland).

The measurements were carried out in the temperature range from -20 to 150°C in air. The measurements were carried out in a dynamic mode with a constant heating rate of 10 deg/min. The mass of the sample used for measurements was 4–8 mg. For the analysis, aluminum crucibles with a volume of 40 μL were used. The weighed sample was placed in a crucible and sealed with a lid using a press.

The glass transition temperature of the polymer was determined from the DSC curve obtained in the heating mode of the sample. Using the tangent method, the middle of the bend (step) on the curve was determined, which was taken as the glass transition temperature.

2.3.3. Determination of Mushroom Resistance of Samples of PVC Films.
Determination of mushroom resistance of the samples was carried out according to the state standard 9.049-91 (ISO 846-78) Unified system of corrosion and ageing protection.

Polymer materials and their components. Methods of laboratory tests for mould resistance. For this, three species of mycelial fungi were used, which are the main biodestructors of various materials, including polymeric ones: Aspergillus niger, Pénicillium sp., and Paecilomyces sp. A suspension of fungus spores with a spore concentration of each fungus species of 1–2 ppm/cm³ was used.

Samples of PVC films of size 3.0×3.0 cm and thickness 1.0 ± 0.2 mm were purified from external contaminants by immersion for 1 min in ethanol and then dried. The samples thus prepared were placed in sterile petri dishes.

For study, the films were infected with mold fungi spores in a solution of mineral salts with sugar (Chapek–Doks medium): The surface of the samples was uniformly sprayed with a suspension of fungi spores, preventing the droplets

from draining, kept in the box until the droplets dried, and the PVC film surface was treated on the other side in a similar way.

Test samples of films in glass petri dishes were kept under optimal conditions for the development of fungi, in a thermostat at a temperature of 30°C for 28 days with intermediate inspection after 7 and 14 days.

After 5 days, control petri dishes were examined for the viability of fungal spores. Subsequently, after every 7 days, the exciter cover was opened for 3 minutes with inflow air.

During the intermediate examinations and at the end of the tests, samples were removed from the chamber or exicator, examined with the naked eye in scattered light at an illumination of 200–300 Lx, and at an increase of 56–60 times. Mushroom resistance was assessed by mushroom development intensity of samples on a 6-point scale. Samples without treatment with microscopic fungi acted as controls.

The material is considered to have passed the test if fungi are found on its surface, the intensity of development of which is estimated at no more than three points on a 6-point scale.

If the relative error and the probability of the arithmetic mean of the fungal development indicator falling within the confidence interval are not specified, the number of samples per sampling must be at least seven.

Sampling for the quantitative determination of the indicator of the development of fungi on the material is carried out at intervals of once a day. The number of selections must be at least seven.

If the difference between the average with the minimum or maximum experimentally obtained values exceeds 50%, it determines the fungal resistance a new series of samples.

For the test result, the maximum score is taken, which is established for five samples. The tests are repeated on new samples taken from the same batch of material.

Statistical processing of the obtained data was carried out using the computer program Excel 2007, calculating the average arithmetic and standard error of the average. The validity of differences between mean values was evaluated by Student's t-test at significance level $a = 0.05$.

2.3.4. Determination of Water Absorption of Samples of PVC Films. Water absorption Δm (%) was evaluated according to state standard 4650–2014 "Plastics. Methods for the determination of water absorption"[62]. For this, the change in the mass of the samples during exposure to distilled water at a temperature of (23 ± 2)°C for certain time intervals was determined by Formula (3):

$$\Delta m = \left[\frac{m - m_0}{m_0} \right] \bullet 100\%, \tag{3}$$

where m_0 and m are the initial mass of the sample and at the certain time, respectively.

The test was carried out for each point on three samples.

2.3.5. Determination of Indicators of Tensile Stress and Elongation at Break of Samples of PVC Films. Determination of indicators of tensile stress and elongation at break (state

standard 9998–86) [63]: samples are secured to the clamps of the testing machine. They are uniformly tightened so that the specimen does not slip during testing, but the specimen is not destroyed at the fixed point. Tests are carried out at a temperature of (23 ± 2)°C and relative humidity (50 ± 5) %.

Tensile strength (MPa) is calculated by Formula (4):

$$\sigma_z = \frac{F_{\max}}{A_0}, \tag{4}$$

where $F_{\max}$ is the maximum tensile load during the tensile test, N; A_0 is the initial cross-section of the sample, mm^2.

Elongation (%) is calculated by Formula (5):

$$\varepsilon_r = \frac{\Delta l_{0r}}{l_0} \bullet 100, \tag{5}$$

where l_0 is the initial calculated sample length, mm; Δl_{0r} is the change in the estimated length of the sample at the time of rupture, mm.

2.4. Preparation of Film Samples. The following compositions were prepared for testing:

(1) 100 parts by weight of PVC, 42 parts by weight of the plasticizer DOP, and 3 parts by weight of calcium stearate stabilizer

(2) 100 parts by weight of PVC, 42 parts by weight of a mixture of plasticizer DOP: DPEA in a ratio of 35 : 7, and 3 parts by weight of calcium stearate stabilizer

(3) 100 parts by weight of PVC, 35 parts by weight of a plasticizers DOP, 7 parts by weight of a plasticizing composition with DPEA and zinc compound, and 3 parts by weight of calcium stearate stabilizer

To obtain the test samples, the ingredients of the PVC composition were mixed in a two-stage laboratory mixer for 60 minutes. To study the PVC composition, samples were obtained in the form of rigid and plasticized films. PVC film samples were obtained by rolling on laboratory rollers at temperatures of 165–175°C for 5 minutes.

3. Results and Discussion

3.1. Synthesis of Ethoxylated Phenol. The phenoxyethanol production reaction has been well studied and carried out on an industrial scale [64, 65]. Ethoxylated phenol was synthesized according to published procedures [66].

3.2. The Synthesis of Decyl Phenoxyethyl Adipate (DPEA). Previously, we have prepared adipates of ethoxylated alcohols by an esterification reaction in the presence of homogeneous catalysts, described their properties, and studied the possibility of using them as nontoxic plasticizers of polyvinyl chloride [67, 68]. Using a heterogeneous zinc oxide catalyst, we have prepared and described in [69] the plasticizing composition comprising butoxyethyl phenoxyethyl adipate and

zinc phenoxyethyl adipate. This paper discusses a synthesis method using a heterogeneous zinc oxide catalyst of the novel plasticizing composition comprising decyl phenoxyethyl adipate and zinc decyl adipate.

Use of this catalyst for preparing the developed plasticizing composition is due to the possibility of using zinc oxide for production together with the plasticizer in one reaction mass of zinc carboxylate. The resulting plasticizing composition in the PVC plastic composition provides a complex action. In addition, the production process avoids additional steps of neutralization and purification of the obtained product and improves its quality.

The target ester was obtained in two stages (see Scheme 1).

Initially, an adipic acid monoester was prepared. Decanol was reacted with adipic acid taken in the equimolar ratio in the presence of toluene solvent and zinc oxide catalyst in an amount of 1 wt% of the total component load. Furthermore, without isolating the monoester, a calculated amount of phenoxyethanol was added. The synthesis conditions were selected based on preliminary experiments. The article presents the most optimal conditions for obtaining target products with maximum yields. At the beginning of the synthesis, the reaction mass was heated to a temperature of $110 \pm 10°C$. During the synthesis, the temperature gradually increased to $130°C$. The control was carried out by the acid number of the esterificate, and the end of the reaction was determined by the amount of released water: upon receipt of monoester, 18 g, then upon receipt of diester, 0.93 mol, which is 16.74 g. The reaction mixture was cooled, the product filtered, and dried at $125°C$. The obtained end product is the plasticizing composition consisting of the mixture of decyl phenoxyethyl adipate and zinc phenoxyethyl adipate.

In general, the process was characterized by several parameters:

(1) According to the acid number of the esterificate

(2) By the amount of released water

(3) According to the ether number of the obtained and isolated target product

For further studies, the bulk of the resulting product was carefully separated from zinc phenoxyethyl adipate, and decyl phenoxyethyl adipate was isolated. For this, the resulting product was treated three times with a mixture of solvent water : ethanol = 1 : 1 while heating to 50–60°C. The recovered plasticizer was dried in a vacuum oven. The purity of the product was further confirmed on the DSC thermogram by the number of peaks: There was one peak on the DSC thermogram of the purified DPEA plasticizer. The remainder of the plasticizing mixture was used to obtain PVC plastic and to analyze the biodegradability of the developed additives. Physicochemical properties of the decyl phenoxyethyl adipate are shown in Table 1.

At the next stage of work for the practical application of the developed decyl phenoxyethyl adipate as a plasticizer, PVC composites identified the main technological indicators: thermal stability, melting and crystallization temperatures, and compatibility with the polymer.
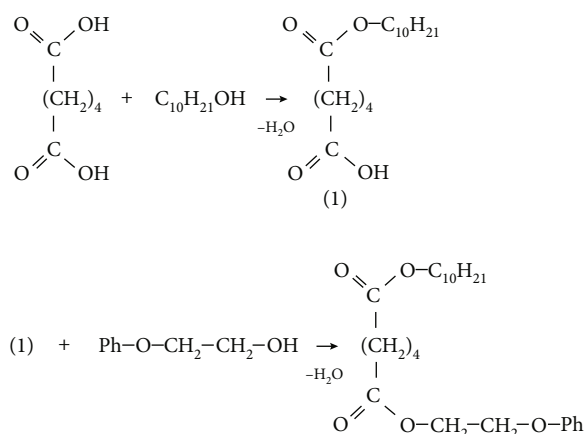
Scheme 1: Synthesis of decyl phenoxyethyl adipate (DPEA).

The thermal stability of the resulting plasticizer was studied by thermogravimetry using a TGA-DSC-Combined Thermal Analysis (Mettler Toledo) apparatus in a temperature range of 20–500°C at a heating rate of 5°C/min (see Figure 1). An industrial plasticizer of di-2-ethylhexyl phthalate (DOP) was used as a reference.

An important indicator for using a plasticizer in processing together with PVC is the change in the weight of the additive when heated under similar temperature conditions. The obtained results of heating the plasticizer to temperatures of 180°C and 200°C, respectively, are shown in Table 2.

The results of the thermal analysis showed that the decomposition of the developed DPEA plasticizer occurs in the temperature range from 101 to 375°C (see Table 2). The highest rate of change in the mass of the sample was observed at a temperature corresponding maximal value. The obtained decyl phenoxyethyl adipate is characterized by a high decomposition start temperature $T = 101°C$. However, this parameter is somewhat inferior to that for industrial DOP (see Table 2).

Important for the use of decyl phenoxyethyl adipate as PVC plasticizer is the relatively low values of the parameter Δm of the test additive at temperatures of 180 and 200°C. These values characterize the content of volatile impurities in the resulting product, which can be released from the processing of the plasticized PVC composition during the formation of materials and products. For the DPEA plasticizer, the obtained Δm value at 180°C was 0.8% compared to the industrial DOP of 1.0% (see Table 2).

The DTG thermogram of the resulting DPEA plasticizer (see Figure 2) shows the boundaries corresponding to the change (decrease) in sample weight when heated. By the peak area, one can judge the intensity of the decomposition process. The peak maximum corresponds to the highest rate of weight reduction (decomposition) of the sample. According to DTG curves, the main peak of thermal destruction of the DPEA is about 316.50°C, while for an industrial DOP plasticizer, this value is 284.83°C (see Table 2). From DTG curves, it can also be observed that DPEA exhibits a one-step degradation behavior.

Table 1: Physicochemical properties of decyl phenoxyethyl adipate (DPEA).

| Ester | Molecular weight | Indicators | | d^{20}_4 |
		Acid number, mg KOH/g	Ester number, mg KOH/g	
DPEA	407	0.1	275	0.9957

Thus, the DPEA plasticizer is characterized by thermal stability values close to the industrial DOP plasticizer.

However, unlike DOP, the synthesized plasticizer is a solid product; therefore, the melting point and crystallization are important indicators for its practical use.

The DSC thermogram of the plasticizer obtained in the heating mode of decyl phenoxyethyl adipate shows an endothermic peak corresponding to the melting of the product. This process corresponds to a melting peak at a temperature of 84°C, for which $\Delta H_m = -67.78$ J/g.

The DSC thermograms, obtained upon subsequent cooling of the sample, clearly show an exothermic peak corresponding to the crystallization of the plasticizer. The crystallization process is shifted to the region of lower temperature, and the exothermic peak corresponding to this process is of low intensity. Thus, on the thermogram of the product, there is a crystallization peak at a temperature of 8°C, for which $\Delta H_{cr} = 131.24$ J/g (see Figure 3). The crystallization process is always shifted relative to melting to a lower temperature region. At the cooling rate of 10 deg/min, the crystallization process may not be complete. In addition, other different factors may influence the melting and crystallization processes. Therefore, there may be a marked difference in the temperatures and enthalpies of melting and crystallization of the products.

Values of the enthalpy of melting ΔH_m and crystallization ΔH_{cr} corresponding to the indicated peaks in the DSC thermogram are given in Table 3.

The reliability of the plasticizer is largely determined by its ability to be retained in the polymer for a long time, that is, the compatibility of the plasticizer with polyvinyl chloride. This characteristic of the developed product is an important parameter for the possibility of using the obtained decyl phenoxyethyl adipate as a plasticizer in polymer compositions since it provides the possibility of obtaining a well-plasticized material. The resulting plastic should not change its composition for a long time; that is, the plasticizer should not vent, evaporate, and volatilize or modify the original composition. One way to determine the compatibility of the plasticizer with PVC is to evaluate the critical dissolution temperature of the polymer in the plasticizer. Tests showed that the dissolution temperature of PVC in the developed DPEA plasticizer was higher (56°C) than in DOP (see Table 4), indicating a lower compatibility of this compound with the polymer. Probably, the obtained decyl phenoxyethyl adipate can be referred to as secondary plasticizers, which are partially compatible with the polymer and are used as a mixture with a primary plasticizer, for example, with DOP.

Therefore, for further work, a mixture of DOP with the synthesized plasticizer DPEA in the ratio of 5 : 1 (wt.) was obtained. The compatibility of PVC with this mixture of plasticizers ($T_c = 119$°C) is slightly lower than with DOP (see Table 4); however, this mixture can be used as part of PVC composites.

To study the effect of the DPEA plasticizer and the developed zinc decyl adipate additive on the biodegradation of PVC plastics, PVC films with compositions 1, 2, and 3 were tested (paragraph 2.4).

Initially, a mycological test was used to assess the biostability of the obtained film samples. It was found that in the first week of incubation on the sample of composition 2, the initial growth of mold cultures occurs with the formation of foci of mycelium and the formation of sporulation. Furthermore, active growth of micromycete colonies occurs, as a result of which the material of composition 2 was covered with molds, which indicates the presence of an available substrate in the system and confirms the bioavailability of the developed composite for various genera of microscopic fungi. Fouling of the sample of composition 2 is observed already on the 14th day of infection, and the process of fungal growth continued throughout the experiment.

When testing a sample of composition 1, there was a slight growth of moldy cultures with the formation of foci of mycelium.

For the samples of composition 3, no growth and development of foci of mycelium of molds occurred during the entire period of the experiment (28 days).

The assessment of the biostability of the developed composites was carried out on the 28th day of the experiment (see Table 5).

At the end of the incubation period, it was found that polymer compositions 1 and 2 are capable of being used as a food source for microscopic fungi such as *Aspergillus niger*, *Pénicillium funiculosum*, and *Trichoderma lignorum*. Therefore, the materials contain sufficient amounts of nutrients to support the growth of fungi.

However, when composite 3 was tested for 28 days, no growth of mycelium of molds with the development of sporulation was observed.

Practically, all materials are susceptible to biodamage. The degradation of most organic materials, regardless of origin, is due to the ability of microorganisms to use the polymer as a whole or its individual components as a carbon and energy source [71–73].

For bioresistant materials that do not have biocidal properties, contamination causes fouling, clogging, and damage by fungi. Of microorganisms, mycelial fungi have the greatest damaging effect on polymeric materials. The fungus spore, falling on a material that does not contain food sources for the microorganism, is able to sprout and form microcolonia only due to the nutrients contained in the spore itself. Further growth of the mycelium will be facilitated by substances polluting the material—the remains of plants, insects, and soil particles. Fungal metabolism products alter the structure of the material, making it available to microorganisms.

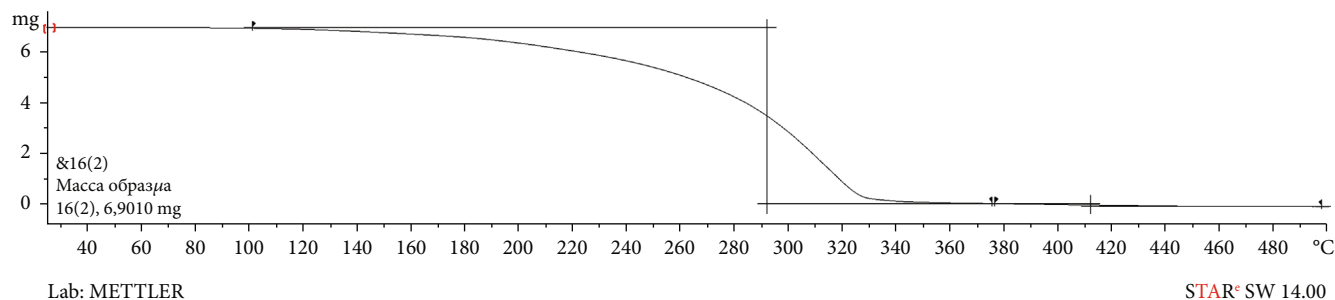Plasticizers included in PVC-based materials are characterized by different resistances to microorganisms. At the

Figure 1: TGA curve of the plasticizer of DPEA.

Table 2: The results of the thermal analysis of plasticizers.

| Sample | Characteristics | | | | |
| | Temperature, °C | | | Δm, % | |
	Beginning	Maximal value	End	At 180°C	At 200°C
DPEA	101.35	316.50	75.44	0.8	1.6
DOP	134.07	284.83	97.89	1.0	1.9

same time, the nature of the plasticizer plays an important role. When microorganisms use plasticizers as a carbon source in PVC materials, significant changes in properties are observed.

It is known that, unlike phthalate plasticizers, adipate plasticizers are involved in the process of life of various microorganisms, as a result of which acidic products soluble in water are formed. For example, oxalic, succinic acids which provoke the acceleration of the decomposition process of the material [56, 74, 75].

Degradation of polymer materials in natural conditions is a complex process, the speed of which is influenced by the structure and properties of the polymer material and the surrounding conditions—humidity, temperature, acidity of the medium, and light, as well as contact with the soil and soil type. The ability of PVC plastics to biodegradate under natural conditions is primarily characterized by a change in the mass of samples in water at room temperature. The effect of migration of plasticizers on the bioavailability of polymer materials was confirmed by data obtained from the long-term exposure in soil of PVC compositions by changing the modulus at 100% deformation. As the plasticizer content in PVC composition increases, the changes increase markedly [76].

In this case, the change in the weight of the PVC composites 2 and 3 containing the DPEA plasticizer is initially due to the washing out of the adipate plasticizer. Subsequently, the change in mass is the result of two opposite processes: initially, a slightly greater reduction in the weight of the sample of formulation 3 is probably due to the better solubility of zinc carboxylate. The sample corresponding to composition 1 is much less susceptible to weight change because the DOP is incapable of washing out (see Figure 4). The greater leaching of plasticizers from films 2 and 3 is probably due to the presence of polar C–O–C groups in their structure, which are available for interaction with water, in contrast to DOP. The liquid phase in contact with the films was evaporated after

the experiment at 50°C and atmospheric pressure to a "the dry residue", which was weighed.

In the work, the study of biodegradation of the obtained samples was carried out while holding them in soil under natural conditions at a depth of 15 cm for 350 days. The temperature regime corresponds to the local climatic zone and is $-30 \cdots +30°C$.

The physical and mechanical properties of the PVC material change significantly due to the degradation and washing out of the DPEA plasticizer in composition 2. Figure 5 shows the nature of the change in the most important operational properties of film materials at the time of action of microorganisms in full-scale tests. The increase in tensile strength and the corresponding decrease in strain at break indicate a reduction in film elasticity due to degradation and loss of part of the plasticizer.

It is known that the bioavailability of polymeric materials during aging is raised. Aging and biodamage of polymers are interconnected and stimulate each other. For this reason, inhibition of one of the processes contributes to a decrease in the rate of the other. Currently, there is a wide range of technological methods that make it possible to purposefully regulate the bioavailability of polymer composites [77, 78]. When choosing biocidal excipients, their suitability in terms of resistance to increase temperature effects and consumption by microorganisms as food products, as well as their low cost and availability, should be taken into account.

For PVC film samples, according to formulation 3, physical and mechanical stability is characteristic at the initial stage. After the expiry of the zinc decyl adipate additive (280 days), a significant change in film elasticity is observed, due to the influence of a biodegradable adipic acid plasticizer. Perhaps this fact indicates the biocidal action of the zinc ion, which is part of the resulting carboxylate.

Phthalate plasticizers are not a nutrient medium that ensures the life of microorganisms in the soil. Therefore, in the case of composition 1, as expected, no noticeable changes in the physical and mechanical properties of the PVC film were found. A slight increase in film elasticity of composition 1, accompanied by a decrease in tensile strength, is likely due to the film's absorption of soil microorganism life products.

The results obtained in this work are in good agreement with the data obtained in the article [79], which studied the damaging effect of inorganic zinc salts on 6 probiotic preparations based on bacteria of the genus Bacillus that was
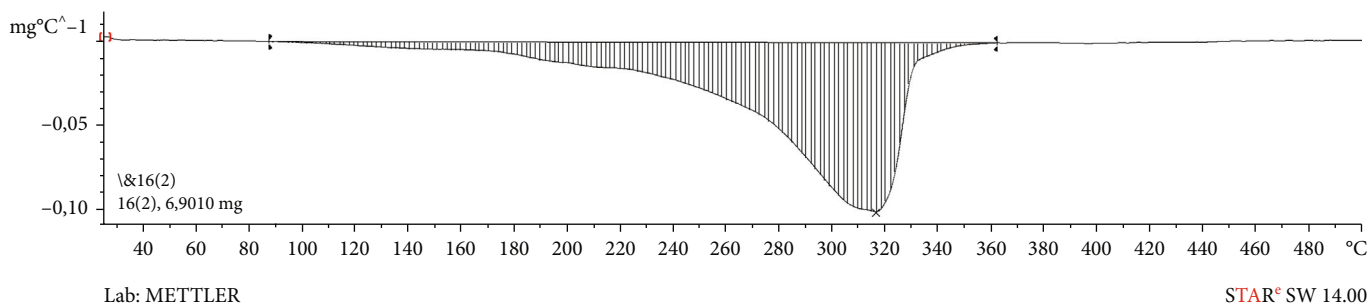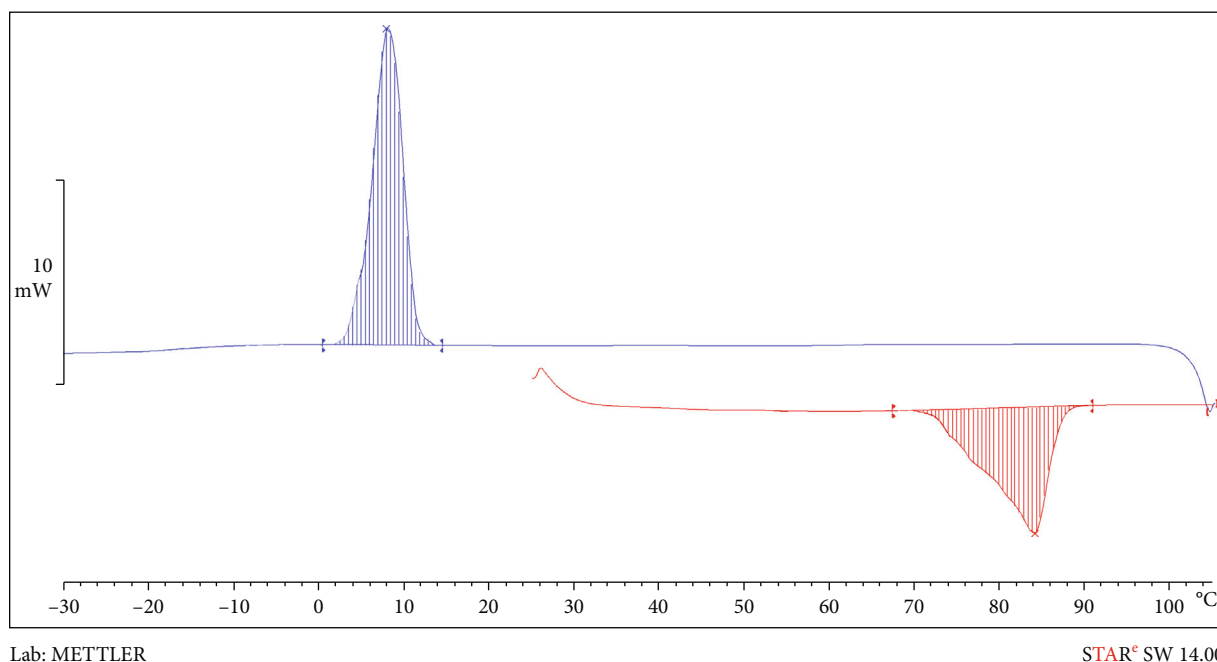
Figure 2: DTG curve of the plasticizer of DPEA.

Figure 3: DSC thermogram of a plasticizer of DPEA.

Table 3: DSC analysis of decyl phenoxyethyl adipate plasticizer.

Sample	Endotherm characteristics				Exotherm characteristics			
	Temperature, ˚C			ΔH_m, J/g	Temperature, ˚C			ΔH_{cr}, J/g
	Beginning	Maximal value	End		Beginning	Maximal value	End	
DPEA	75.61	84.00	86.88	−67.78	11.31	8.00	4.67	131.24

Table 4: The results of determining the critical temperature of the dissolution of plasticizers.

Plasticizer	T_c, ˚C
DOP	113
DPEA	169
Mixture DOP: DPEA (5 : 1)	119

Table 5: Evaluation of the biostability of PVC composites in points.

Composition number	Aspergillus Niger	Micromycete Pénicillium funiculosum	Trichoderma lignorum
1	1	1	1
2	4	4	4
3	0	0	0

studied: Sporobacterin (B. subtilis 534), Bactisubtil (B. cereus IP 5832), Vetom 1.1 (B. subtilis 10641), Vetom 2 (B. licheni-formis 7038), Vetom 3 (B. amyloliquefaciens 10642), and Vetom 4 (B. amyloliquefaciens 10643). It was found that zinc acetate has the most pronounced toxic effect on the studied microorganisms. However, the values of the zones of growth
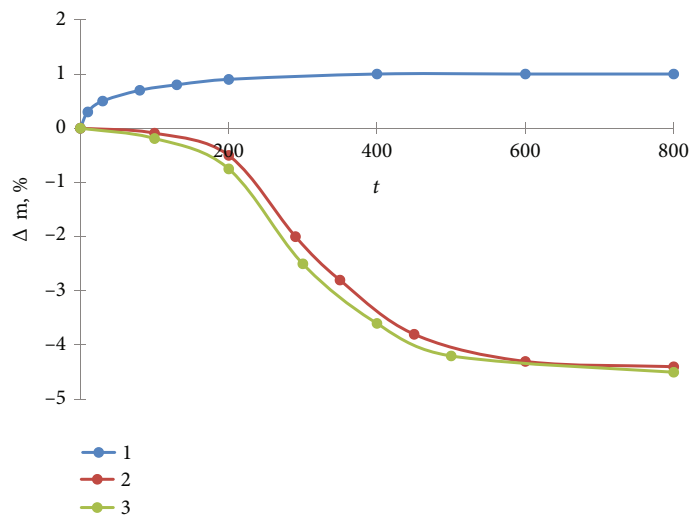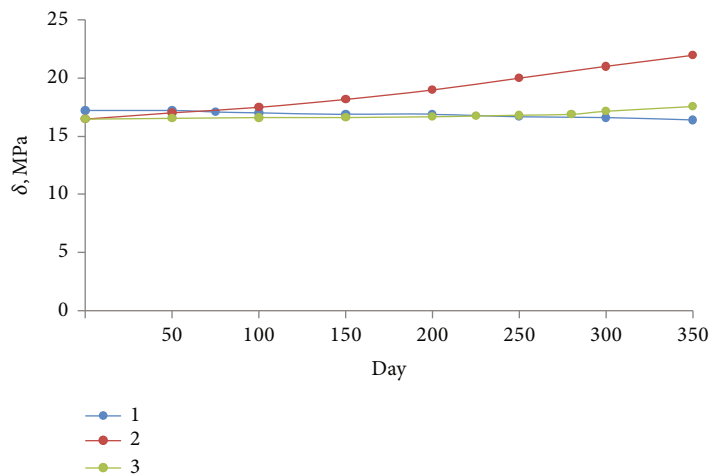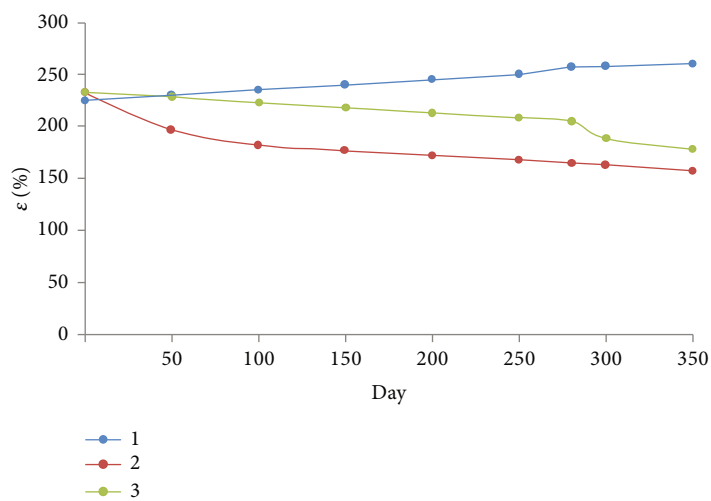
Figure 4: The change in mass (Δm) as a function of time (hours) in water for PVC film samples.

(a)

(b)

Figure 5: The change of physical and mechanical properties of plasticized PVC films during full-scale test: (a) Tensile breaking stress. (b) Elongation at break.

inhibition under the action of this compound slightly exceeded the values of sulfate, chloride, and zinc nitrate for the probiotic strains under study. It was also found that B. cereus 5832 was the most resistant to zinc nitrate, B. subtilis 10641 zinc sulfate, zinc acetate ,and B. cereus 5832 zinc chloride. Although such inorganic zinc compounds, according to the results obtained in this work, they are quite effective as a biocidal preparation, and the plasticizing additive we have developed in the PVC composition provides several functions: plasticization, lubrication effect, and biocidal action.

The zinc-containing biologically active polymers [80–83] obtained by polymeranalogous transformations are effective, but they have disadvantages that do not contribute to their widespread use: complex synthesis of a biocide, involving several stages; inhomogeneities in the composition of the modified polymer make it difficult to create polymers with a predetermined set of properties.

Another work described the preparation of two structurally different zinc-based coordination polymers with excellent antibacterial activity [83]: The first, $[Zn(bipy)(OH_2)_4^{2+}]_{1.5}[ClO_4^-]_3$ $(bipy)_3(H_2O)$, consists of a one-dimensional (1D) structure with two crystallographically independent octahedral zinc centers transcoordinated by two $4,4'$-bipy units and water groups. The second, $[Zn_{1.5}(CH_3CO_2)_2(bipy)_2^+][ClO_4^-] H_2O$, is a two-dimensional (2D) layered structure with the same polymers but bridged together into a layer by acetate and $4.4'$-bipy. Due to the slow release of Zn^{2+} ions during their gradual decomposition in aqueous solution, they provide highly effective antibacterial activity against Escherichia coli and especially against Staphylococcus epidermidis cells. Such polymers have their own applications, and the toxicity of these coordination polymers depends not only on the zinc cation but also on the ligand that is part of the composition. In our case, the developed additive ensures the production of PVC compositions with a certain service life and accelerated decomposition after the end of operation under natural conditions. In addition, it is important that the additive is synthesized on the basis of nontoxic adipic acid and is environmentally friendly and biodegradable.

4. Conclusions

Studies have shown that the following factors contribute to changing the structure of film samples of developed PVC compositions: migration of a plasticizer from a film sample, diffusion into films of soil moisture, and washing out of samples of low-molecular ingredients and microbiological impact of microorganisms present in the soil. The magnitude and nature of these changes directly depend on the nature of the introduced plasticizer.

The laboratory studies of the biostability of the obtained film samples in relation to the most destructive microorganisms showed that the samples of composition 2 containing an adipate plasticizer are most susceptible to biofouling by micellial fungi and, therefore, are involved in the process of their vital activity, since they are a nutrient medium for molds. In samples of PVC composition 1 based on DOP, an insignificant overgrowth with microscopic fungi was observed, which is associated with extraneous sources of carbon nutrition, that is, with the presence of contaminants. In the samples of film 3, after the experiment lasting 28 days, no growth of the mycelium of molds with the development of sporulation was observed.

According to the data obtained as a result of field experiments for 350 days, the greatest change in the physicomechanical parameters of the film samples was observed in PVC composition 2 with the content of an adipate plasticizer: the tensile breaking stress increases, and the elongation at break decreases by approximately 30%. For samples of film 1 based on DOP, no significant changes in physical and mechanical parameters were observed during the experiment. PVC composition 3 with the content of the zinc compound and the developed plasticizer for a certain time (approximately 280 days) under ambient conditions retained its initial physical and mechanical properties, that is, did not undergo significant changes. This fact is probably associated with the biocidal action of the zinc compound. Intensive biodegradation of film samples began after a certain period, which is explained by the migration of this additive into the soil. The tests carried out on water absorption for 800 h for film samples confirm the decrease in the mass of samples 2 and 3.

Thus, it can be argued that the partial replacement of the industrial plasticizer DOP with a new biodegradable plasticizer decyl phenoxyethyl adipate accelerates the biodegradation of used PVC products under natural conditions.

At the same time, the service life and initial physical and mechanical properties of PVC composites based on the developed plasticizer are not inferior to industrial plastics based on DOP. The new zinc decyl adipate additive enables to obtain biologically decomposable thermoplastic PVC compositions with a controlled service life. Application of the developed plasticizing composition in the composition of PVC plastics is a promising method of reducing the amount of polymer waste and improving the environmental situation.

Data Availability

The data used to support the findings of this study are included within the article: Patent 2716691 RU, Int. Cl. 51 C08L 27/00 (2006.01) Plasticiser for compositions based on polyvinyl chloride. Mazitova A.K., Aminova G.K., Vikhareva I.N., Sukhareva I.A., Zaripov I.I., Akhmetov I.R. Proprietor Federalnoe gosudarstvennoe byudzhetnoe obrazovatelnoe uchrezhdenie vysshego obrazovaniya "Ufimskij gosudarstvennyj neftyanoj tekhnicheskij universitet" (RU)–No. 2019131313; date of filing 02.10.2019; date of publication 13.03.2020.

Conflicts of Interest

The authors declare no conflict of interest.

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