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Evaluation of the efficiency of using new environmentally friendly PVC additives based on adipic acid

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ABSTRACT: Introduction. The economic activity of a person entails environmental, economic and social damage to the environment. The production of goods or services is associated with the consumption of natural resources and emissions that negatively affect the ecological state. Currently, there is an acute problem of the negative impact of man on the natural environment and is the main source of deterioration in the health of living beings. In modern conditions, chemical safety is one of the priority tasks of socio-economic development. To protect the environment, it is important to take appropriate measures and develop appropriate mechanisms to promote sustainable development. For this purpose, an assessment of the environmental and economic damage from human activities is required. **Materials and methods.** The work employs the method for determining the prevented environmental damage, approved by the Chairman of the State Committee of the Russian Federation for Environmental Protection, to perform ecological and economic assessment of the environmental impact of new environmentally friendly biodegradable additives for polyvinyl chloride based on adipic acid. **Results and discussion.** Polymeric materials, as the most popular and widespread, make a significant contribution to the deterioration of the environmental situation. In this regard, the main values of the prevented environmental damage from soil degradation were calculated when using new environmentally friendly additives for PVC based on adipic acid. **Conclusion.** The introduction of the developed additives into the composition of the developed additives provides economic and environmental efficiency in order to accelerate the biodegradation of polymer composite materials, protects against chemical pollution by hazardous toxic compounds and helps prevent soil degradation.

KEYWORDS: adipate plasticizer, biodegradable, economic efficiency, environmental damage, polyvinyl chloride.

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INTRODUCTION

An improvement in the set of properties of large-scale synthetic polymers was achieved due to an increase in the efficiency of synthesis conditions, targeted regulation of their molecular weight and molecular weight distribution at the nano-, micro- and macrolevels. An important factor in solving this problem was the improvement of the technology for the production of plastics based on improved polymer components and the improvement of methods for preparing raw materials, methods and techniques for mixing compositions.

Since the 1950s, there has been a stable global growth trend in the plastics market: from 1 million tons in 1950 to 348 million tons in 2017 year [1].

In connection with the increasing volumes of production and consumption of polymer materials and products, an important environmental problem is the constant increase in the huge amount of plastic waste. Thanks to this, a separate direction has been formed – the recycling of plastics, in which specific combinations of technological processes are used, which contributes to the solution of environmental and raw material problems, in particular. Chemical depolymerization processes make it possible to produce raw materials for obtaining monomers, oligomers, and other chemical materials using economically viable methods [2–8].

However, to date, the disposal of polymer products after operation most often occurs at solid waste landfills or is spontaneous.

Soil pollution leads to degradation of the soil cover, withdrawal of land from agricultural use and significant financial costs for the implementation of measures for the remediation of contaminated land.

Soil contamination with waste polymer materials poses a significant hazard due to the toxicity of some additives, as well as the migration ability of individual components.

Thus, it is extremely important today to develop polymer composite materials with a controlled service life, which are characterized by the stability of operational characteristics during the entire period of their use, and then degrade naturally under environmental conditions with the formation of non-toxic substances.

MATERIALS AND METHODS

Calculation of the prevented environmental damage from soil degradation when using the developed adipate additives

Economic damage to the environment is the actual and possible losses caused to the national economy by pollution, expressed in value terms, or additional costs to compensate for these losses.

Economic damage from the deterioration and destruction of soils and lands under the influence of anthropogenic (technogenic) loads is expressed in land contamination with chemicals; littering of land by unauthorized landfills, other types of unauthorized and unregulated disposal of waste and the accompanying degradation of soil and land.

Degradation of soils and lands is a combination of natural and anthropogenic processes leading to changes in the functions of soils, quantitative and qualitative deterioration of their properties and composition, and a decrease in the natural and economic significance of lands. The extreme degree of degradation is the destruction of soil cover and damage to land.

These are the main types of soil and land degradation:

– technological (operational) degradation – mechanical destruction of the soil cover due to open and closed mining of minerals and peat, as well as construction and geological exploration: disturbance of land, physical degradation, agrodepletion;
– erosion – destruction of the soil cover under the influence of surface runoff and wind, followed by the movement and relocation of soil material: water and wind;
– salinization – the accumulation of water-soluble salts, including the accumulation of sodium and magnesium ions in the soil absorbing complex: salinization and alkalinization itself;
– waterlogging.

The degree of soil and land degradation is determined using indicator indicators, for which threshold values have been established to determine the loss of the natural and economic significance of lands. Degradation of soils and lands for each indicator is characterized by degrees from 0 to 4.

Loss of annual income is taken into account when calculating the amount of damage from soil and land degradation inflicted on their owner. Its amount is calculated at the current prices at the time of determining the amount of damage.

Economic effect – the difference between the results of economic activity (for example, a product in value terms) and the costs incurred to obtain and use them.

Environmental-economic effect – the ratio of the size of the positive effect (benefit) and harm (damage) caused by the impact on the environment, as well as the amount of costs required to compensate for such damage.

Calculation of the amount of damage caused to soils as an object of environmental protection is carried out according to a certain method. The methodology for calculating the amount of damage caused to soils as an object of environmental protection is intended for calculating in value terms the amount of damage caused to soils as a result of violation of legislation in the field of environmental protection, as well as in the event of emergencies and emergencies of a natural and man-made nature.

The methodology calculates the amount of damage caused to soils as a result of:

a) chemical contamination of soils as a result of the ingress of chemicals or a mixture of chemicals into soils, leading to non-compliance with environmental quality standards for soils, including standards for maximum (approximate) permissible concentrations of chemicals in soils;

b) unauthorized disposal of production and consumption waste;

c) spoilage of soils as a result of unauthorized (illegal) overlapping of the soil surface, as well as the soil profile with artificial coatings and (or) linear objects.

Earlier in work, alkylbutoxyethyl adipates were obtained, their characteristics, important for practical use as PVC plasticizers, were investigated [9].

The assessment of the magnitude of the prevented environmental damage from soil degradation when using the developed adipate additives, namely, butyl, hexyl, octyl and decyl butoxyethyl adipates, was calculated by the formula [10]:

$$У^{п}_{пр_{д}} = У^{п}_{уд_{х}} \times \sum_{j} S_j \times K_{nj},$$

$$У^{п}_{пр_{д}} = 147\,000 \times 1 \times 1.9 = 279.3 \textit{ thousand rubles},$$

where $У^{п}_{уд_{х}}$ – indicator of specific environmental damage to land resources, thousand rubles; $У^{п}_{уд_{х}}$ = 147 thousand rubles / ha (Ufa c., Russia);

S_j – area of land of type j, preserved from degradation as a result of environmental protection, ha; $S_j = 1$ ha;

K_{nj} – coefficient of natural and economic significance of land resources of the j-type, $K_{nj} = 1.9$.

The amount of prevented environmental damage when using the developed additives is estimated by the formula:

$$У^{п}_{пр_х} = У^{п}_{уд_х} \times \sum_j S_j \times K_i^{o} \times K_{nj},$$

$$У^{п}_{пр_х} = 147\,000 \times 1 \times 3 \times 1.9 = 837.9 \textit{ thousand rubles},$$

where $У^{п}_{пр_х}$ – prevented environmental damage from pollution of land resources with a chemical substance of the i-th hazard class during the reporting period, thousand rubles;

S_j – area of land of type j that was prevented from contamination by a chemical substance of the i-th hazard class during the reporting period of time, ha; $S_j = 1$ ha;

K_i^{o} – coefficient taking into account the hazard class of the i-th chemical that is not allowed to enter the soil or eliminated pollution as a result of the implementation of the corresponding direction of environmental protection, $K_i^{o} = 3$.

The total amount of prevented environmental damage to land resources in the region during the reporting period is determined by the formula:

$$У^{п}_{пр} = У^{п}_{пр_д} + У^{п}_{пр_х},$$

$$У^{п}_{пр} = 279.3 + 837.9 = 1117.2 \textit{ thousand rubles}.$$

If the biodegradation of a polymer material under natural conditions takes more than 100 years, then the environmental damage inflicted over a given period of time will amount to 1,117,200 rubles.

Since the obtained composite PVC-plastic compound with the content of adipate plasticizers degrades in the soil in 0.5 years to 10%, the complete biodegradation will be 5 years. The environmental damage caused over a given period of time will be 55860 rubles.

Thus, the prevented environmental damage during the incorporation of biodegradable adipate plasticizers into production for 100 years will amount to 1,061.34 thousand rubles per 1 ha of land.

RESULTS AND DISCUSSIONS

Modern approaches to solving the problem of recycling

In recent years, biopolymers from renewable raw materials have attracted particular attention of researchers. The main reasons contributing to the development of this area: the ability to complete biodegradation in the environment, reduction of hydrocarbon reserves, reduction of waste and compostability in the natural natural cycle, climate protection due to a decrease in the amount of carbon dioxide emitted.

The production volumes of biodegradable polymers, despite the constant growth of their production, are significantly inferior to traditional polymers.

Currently, the production and consumption of bioplastics is only about 1% of the total amount of PM [11].

According to the latest data from the European Bioplastics Institute and the nova-Institute (Hürth, Germany), global production capacity for bioplastics in 2019 amounted to 2.114 million tons [12–13].

Originally biodegradable PMs were mixtures of traditional polymers with starch. Now a whole range of new biodegradable plastics has appeared, differing in production technologies and composition.

Biodegradable polymers are polymers that are prone to degradation initiated by high humidity and microorganisms. To ensure the biodegradation of such polymers, certain conditions are required: pH, humidity and oxygen saturation.

Promising biodegradable bio-based plastics such as polylactides, polyesters, and polyhydroxoalkanoates are currently expensive and not widely available.

One of the most promising methods for creating such materials is the development and implementation of composite materials based on traditional polymers with additives that accelerate the decomposition of the entire composition.

One of the directions of work on regulating the service life of polymeric materials, in particular PVC, is to ensure their biodegradability [14–15].

In [16–22], attempts were made to obtain polymer composite materials with controlled biostability, basic recommendations were given for the creation of biostable polymer compositions that would expand the operational capabilities of polymer materials and extend their service life in different climatic zones.

For this reason, in connection with the increasing environmental requirements, polymeric materials, along with a high set of technological and operational parameters, must be biodegradable.

The development of polymer composite materials that undergo accelerated physicochemical and biological changes in the natural environment due to the introduction of biodegradable additives is one of the potential methods for the disposal of synthetic materials and ensures the release of significant areas of fertile soils and lands from the constantly increasing amount of polymer waste.

Today, polyvinyl chloride in terms of consumption takes the third place after polyethylene and polypropylene, therefore, the development and use of biodegradable additives for these polymers is relevant, which contributes to solving the urgent problem of environmental pollution with plastic waste.

Renewable sources based on plant materials or their production waste to be utilized as fillers for regulating the biodegradability of polymer composite materials are an alternative for the development of economically and environmentally attractive technologies. However, such composite materials are inferior in physical, mechanical, technological and operational characteristics to traditional polymers. For this reason, it is advisable to modify polymer compositions using plasticizers capable of serving as a source of organic substances for microorganisms-destructors under ambient conditions.

The use of natural biodegradable plasticizers with low toxicity and good compatibility with traditional polymers is a growing trend in the development of bioplastics. Epoxidized triglyceride vegetable oils from soybean oil, linseed oil, castor oil, sunflower oil, and fatty acid esters are widely used as natural plasticizers [23]. However, in some applications, a complete replacement with natural-based plasticizers is simply not possible, so a wide range of commercially available biodegradable synthetic plasticizers have been developed over the past decades: esters of adipic, azelaic, sebacic, citric and tartaric acids [24].

For this purpose, it is possible to use biodegradable plasticizers in the formulations of PVC compositions, for example, esters of adipic acid. In addition, PVC composites containing adipates have reduced toxicity. In numerous works, the biotoxicity and the period of biodegradation of the industrial adipate plasticizer DOA were investigated and it was shown that this additive for PVC is non-toxic for various types of living microorganisms and the period of its biodegradation is 6 months [25–26].

Expanding the range of biodegradable additives is a topical effective way to increase the biodegradation of PVC composites. In [9], we described the preparation of asymmetric esters of adipic acid and ethoxylated alcohols, namely, butyl, hexyl, octyl and decyl butoxyethyl adipates. Their characteristics, which are important for practical use as PVC plasticizers, have been studied, and the possibility of their biodegradation under environmental conditions has been shown, the biodegradation process and the main metabolites have been studied.

Plasticizers in PVC-based materials have different resistance to microorganisms. The nature of the plasticizer plays an important role in this. 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 additives are involved in the life of various microorganisms, resulting in the formation of acidic products soluble in water. For example, oxalic and succinic acids, which accelerate the decomposition of the material [27–28]. Further weakening of the polymer structure leads to changes in the molecular weight and mechanical properties of plastic compounds. Residues of polymer molecules are perceived by microorganisms as nutrients, which leads to an increase in their population.

Biodegradation of hybrid polymer composites based on large-tonnage synthetic polymers and biodegradable fillers under the influence of soil microorganisms consists in the repeated passage of stages: surface biocorrosion, the formation of a more porous structure (due to “negative washout” and “consumption” of fillers), internal biocorrosion (due to fixation of micromycetes on internal irregularities), the spread of erosion, fragmentation. As a result, polymeric materials, being organic compounds, are capable of biodegradation, i.e. disposed of.

The ability to accelerate biodegradation of PVC compounds with developed adipate plasticizers is an indisputable advantage of the developed additives. The process of destruction of material when it enters the soil occurs under the influence of microorganisms and is accompanied by a significant drop in its strength. The degradability of polymeric materials in nature depends on the structure of the polymer, the presence of a population of degrading microorganisms, and the environmental conditions that favor their growth. Under the action of free radicals and various microorganisms, the resulting fragments are involved in hydrolytic and redox processes, which leads to a decrease in molecular weight and further simplifies and accelerates the process of biodegradation of polymer plastic compound.

The existence of organisms capable of metabolizing synthetic polymers has been of considerable interest in recent years [29]. In general, studies of biodegradation are focused on polymer composites containing a filler [30–32], which has an accelerating effect on biodegradation, being a source of nutrition for microorganisms in the external environment [33–35].

Despite the fact that polyvinyl chloride is a strong polymer, resistant to abrasion and chemical action, characterized by low moisture absorption, researchers note that the lower the molecular weight of the polymer, the more easily its biodegradation occurs [36–37]. According to Kirbas et al., Pure polyvinyl chloride with a low molecular weight is biodegradable by white rot fungi [35].

Thus, certain types of microorganisms are able to utilize polyvinyl chloride, and the additives present in composite materials significantly accelerate this process [38–40].

CONCLUSIONS

Biodegradation is the most convenient and smarter solution for environmentally friendly and efficient disposal of plastic waste. Currently, no technologies have been developed that allow the utilization of materials based on synthetic polymers by biodegradation on a commercial scale. However, a large number of studies are being carried out in this direction and, taking into account the huge metabolic potential of microorganisms, it is possible to predict soon the development of acceptable, rational and cost-effective technologies for the biodegradation of plastic waste. To date, the prevention of environmental damage directly contributes to the economic effect of the development and introduction into production of biodegradable polymer composite materials. The conducted environmental and economic assessment of the use of new PVC adipate plasticizers shows the effectiveness of their use to accelerate biodegradation processes and to protect the environment from soil degradation.

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Aliya K. Mazitova – scientific management.

Zhan F. Bulatasov – participation in development of curricula and their implementation.

Yuriy E. Sapozhnikov – research concept.

Ilnar I. Zaripov – follow-on revision of the text.

Irina N. Vikhareva – methodology development; final conclusions.

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