Biodegradation chemistry of new adipate plasticizers

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Abstract. Plastics are materials that, in the composition of various municipal solid waste, enter the environment in large quantities. Lightness and strength, the ability to withstand the effects of external factors, long-term use led to their widespread use. However, some of the additives needed to improve the performance of polymer products are highly toxic and pose a serious environmental problem. In this regard, the development of environmentally friendly PVC plasticizers is technically important. The article describes the preparation and study of the properties of ester additives based on adipic acid and ethoxylated butanol. The mechanism of biodegradation of the synthesized adipates was studied, the resulting metabolites were determined. The ecological safety of the developed plasticizers in the process of utilization in natural conditions is shown.

1. Introduction

The raw material for plastic products is a wide range of high molecular weight organic polymers obtained mainly from petroleum [1–2]. Currently, there is a tendency of constant growth in the production and consumption of plastics due to their availability and excellent technical and operational characteristics [3–5]. However, most polymeric materials are not readily biodegradable. On the other hand, the widespread use of plastics, lack of waste management and unauthorized disposal pose a significant threat to the environment [6–7]. These reasons have contributed to the development of innovative methods of plastic waste management and the introduction of biodegradable polymers, especially for disposable products.

Modern methods of recycling polymeric materials are based on chemical, thermal, photo- and biological effects [8]. Managing waste plastics wisely is a challenge.

The urgent need for biodegradable polymers has led to a significant increase in research work in this direction. Some of them have been developed on an industrial scale [9]. However, further improvement of technological (chemical and biotechnological) processes for the production of biodegradable polymers is required. It is important to study the interaction of biodegradable polymeric materials with biological media in order to optimize the decomposition time and ensure their safe use and disposal [10].

Polyvinyl chloride (PVC) is one of the most common plastics in use today due to its low cost, durability, versatility and modifiable properties. Plasticizers are used to impart plasticity to PVC and extend the range of the highly elastic state of the polymer. The share of plasticizers in PVC products varies from 20 to 80% [11].

Ester plasticizers account for approximately 90% of the plasticizers produced. The dominant part is made by phthalic acid esters - more than 80% of the market. These additives are low molecular weight compounds that easily migrate from the polymer matrix. In practical use in medical devices or toys,
contact with biological media occurs and the migration of phthalate plasticizers is significantly accelerated. At the same time, negative changes in the properties of the material are observed, as well as toxic and biological effects of the plasticizer on humans and the environment are possible.

For this reason, the plasticizer market is influenced by the tough directives of the European Council for Plasticizers and Intermediates. According to the examination carried out, PVC products containing dioctyl phthalate have an adverse effect on health. In addition, the introduction of phthalate plasticizers into the formulation of the PVC composition increases the fungal resistance of the resulting material. This property characterizes the possibility of biodegradation in vivo.

Plasticizers based on adipic acid are included in the list of safe substances and are allowed for use in contact with food. Studies have shown that these additives reduce the mushroom resistance of PVC products. However, when developing biodegradable formulations, it is important to know the safety of the additives used and the chemical processes that occur during their biodegradation: the composition of the resulting metabolites and the duration of their existence.

In this regard, the production of esters of adipic acid for possible use as plasticizers of PVC, the study of the process of their biodegradation is an urgent task.

2. The objective of the research

2.1. Starting Materials

Adipic acid (purum 99.8 %) was purchased from Radici Group, Selbitz-Hochfranken, Bavaria, Germany. Butanol (purum 99.7 %), hexanol (purum 98 %), octanol (purum 99 %) and decanol (purum 99 %) were purchased from The Company «Rearus», Moscow, Russia. Ethylene oxide is a white solid with a main substance content of 98.2%, was purchased from ECOTECH Chemical Components Plant, Moscow, Russia. Sodium hydroxide was purchased from Joint Stock Company “Caustic,” Sterlitamak, Russia, it is a white solid with a main substance content of 98.2%. P-Toluenesulfonic acid was purchased from Component-Reagent, Moscow, Russia, it is a white solid, with a main substance content of 95%. Toluene was purchased from Public Joint-Stock Company “Joint-Stock Oil Company Bashneft,” Ufa, Russia. It is a colorless liquid with a characteristic smell a main substance content of 99.9%. Polyvinyl chloride (Joint Stock Company “Caustic,” Sterlitamak, Russia): We used industrial samples of suspension polyvinyl chloride PVC 7059M. 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/cm³, with a residue after sieving on a sieve with a mesh N 0063 – 95%, for the manufacture of plasticized products.

2.2. Synthesis Methods

The synthesis of alkyl butoxyethyl adipates.

Ethoxylated butanol and the desired esters were prepared as described previously [12–13]. Briefly, 150 mL of toluene, 1 mol of ethoxylated alcohol, 3.0 g (1% by weight) of p-toluenesulfonic acid and 146 g (1 mol) of adipic acid were charged into the reaction flask and the temperature was slowly raised to 90–95 °C. Stirring was continued for 1.5 h. The end of the reaction was determined by the acid number of the esterificate.

Then was esterified with aliphatic alcohol (1.2 mol). Boiling was continued for 2–3 h. The reaction mixture was cooled and isolated the target ester. All obtained adipates are the light clear liquids. The purity of esters was determined by HPLC.

The yield of butyl butoxyethyl adipate was 343.5 g (89.0% of theoretical).
The yield of hexyl butoxyethyl adipate was 365 g (90.0% of theoretical).
The yield of octyl butoxyethyl adipate was 365 g (90.0% of theoretical).
The yield of decyl butoxyethyl adipate was 343.5 g (89.0% of theoretical).
2.3 Methods of analysis

2.3.1 Analysis of physicochemical parameters of plasticizer. For the received broadcasts, the following indicators were determined: Acid number, ester number, mass fraction of volatile substances.

Determination of acid number. The method is based on the reaction of neutralization of residual acidity in a plasticizer with an alkali solution. About 50,000 g of plasticizer is weighed in a conical flask and 50 cm$^3$ of ethyl alcohol is poured in with a cylinder. To the resulting solution, add 3-6 drops of phenolphthalein and titrate from the burette with sodium hydroxide solution until a slightly pinkish color appears, stable for 30 sec.

Determination of ester number. The method is based on the reaction of saponification of the ester groups of the plasticizer with 1 mol/dm$^3$ with an alkali solution. A portion of the plasticizer is weighed in a conical flask and 50 cm$^3$ of an alcoholic solution of potassium hydroxide and 5 cm$^3$ of distilled water are added. The flask is connected to a condenser and heated for 1 hour in a boiling water bath. After cooling to room temperature, its inner surface is rinsed through the upper part of the refrigerator with two portions of distilled water, 20 cm$^3$ each, and the contents of the flask are titrated with a solution of hydrochloric or sulfuric acids in the presence of phenolphthalein until discoloration. In parallel, under the same conditions and with the same reagents, but without a plasticizer, a control experiment is carried out.

Determination of mass fraction of volatile substances. (10,000 ± 1,000) g of plasticizer is weighed in a glass previously brought to constant weight at a temperature of (100 ± 2) °C, and placed on asbestos cardboard in an oven, removing the lid. Next, the sample is kept in an oven at a temperature of (100 ± 2) °C for 6 hours. The thermometer is installed in the oven so that the mercury ball touches the asbestos cardboard. Then the glass is taken out and covered with a lid, placed in a desiccator with calcined calcium chloride and cooled for at least 30 minutes. The chilled glass is weighed.

Determination of the density of the plasticizer. The plasticizer to be tested is poured into a clean, dry cylinder along the wall to avoid air bubbles. The level of the plasticizer in the cylinder should not reach its top edge by about 4 cm.

Carefully lower a clean, dry hydrometer into the cylinder, keeping it in hand until it floats without touching the walls of the cylinder. The distance from the hydrometer to the bottom of the cylinder must be at least 3 cm. The reading is made 3-4 minutes after the hydrometer is immersed along the corresponding lower edge of the resin or plasticizer meniscus. When reading, the eye should be at the level of the lower edge of the meniscus.

The density of plasticizers, cloudy or dark-colored, is determined by the division of the hydrometer scale corresponding to the upper edge of the meniscus.

2.3.2 High performance liquid chromatography. The study of the composition of soil samples with utilized adipates was carried out by high performance liquid chromatography (LC-10 from SHIMADZU, Kyoto, Japan) in a reversed-phase mode. The separation of the mixture components was carried out on a column (150x4.6 mm) filled with a Separon-C18 sorbent with a particle size of 5 μm in an acetonitrile-water eluent system, taken in a 67/33 volumetric ratio. The eluent flow rate is 0.5 ml/min. A refractometric model detector (RIDK 101, Prague, Czech republic) was used as a detector. The volume of injected samples was 10 μL. Quantitative analysis was performed using the absolute calibration method. The calibration solutions contained adipic acid, alcohols, and esters.

2.3.3 Characterization of esters of adipic acid. Samples of the obtained products were analyzed by FTIR spectroscopy (KBr tablets), which were prepared according to a standard procedure. IR absorption spectra were recorded in the range 450–3700 cm$^{-1}$ using an FTIR-8400S FTIR spectrometer (Shimadzu, Japan) at room temperature. Resolution – 4 cm$^{-1}$, number of scans – 20.

2.3.4 The study of fungal resistance of adipates. The sample is contaminated with mold spores in water and kept in a box at a temperature of 25 ± 10 °C and a relative humidity of up to 80% until the drops
dry, but not more than 60 minutes. The samples and the control are placed in a chamber, at the bottom of which water is poured. The camera is closed. The tests are carried out at a temperature of 29 ± 2 °C and a relative humidity of more than 90%. The duration of the tests is 28 days with an interim examination after 14 days. Every 7 days, the lid of the desiccator is slightly opened for 3 minutes to allow air to flow. During inspections and at the end of the experiment, the samples are examined with the naked eye in diffused light at an illumination of 2000-3000 lux and at a magnification of 56-60 times. Fungus resistance is assessed by the intensity of development of fungi on the samples on a 6-point scale.

2.3.5. Study of biodegradation of adipates in soil. For testing, the obtained esters were mixed with soil in a ratio of 10 g of ester per 1 kg of soil. At certain intervals, samples of artificially contaminated soil were taken in an amount of 5 g and the content of metabolites in it was determined. For this, extraction was carried out with chloroform 3 times, 20 mL each. The solvent was evaporated. The analysis of the dry residue was determined by the HPLC method.

2.4. Preparation of film samples
The following composition was prepared for testing: One-hundred parts by weight of PVC; 50 parts by weight of the plasticizer; 3 parts by weight of calcium stearate stabilizer.

To obtain test samples, all the ingredients of the PVC composition were mixed in a two-stage laboratory mixer for 60 min. 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 min.

3. Results and discussion
The synthesis of esters of adipic acid and ethoxylated alcohols.

The synthesis and properties of butoxyethanol are given in [12]. Characteristics of the obtained butoxyethanol: density – 0.9648, refractive index – 1.4267, molecular weight (calculated) – 118, yield – 90.5%, reaction time – 0.5 h.

Synthesis of target esters by sequential esterification of adipic acid in one reaction volume (scheme 1). Initially, the reaction mass was loaded with a higher molecular weight alcohol in an equimolar ratio of the starting reagents. To facilitate the removal of released water, the synthesis was carried out in a toluene medium. The duration of the synthesis was controlled by the acid number of the esterificate. Then another alcohol was loaded into the reactor in the ratio acid: alcohol = 1: 1.2. Isolation of adipates was carried out according to the method described in [12]. Unsymmetrical esters of adipic acid were obtained with a yield of more than 80%.

![Figure 1. Synthesis of alkyl butoxyethyl adipates. where R² = [CH₂ − CH₂ − 0] – C₄H₉, R² = butyl, hexyl, octyl, decyl.](image)

The physicochemical properties of the obtained adipates are presented in table 1.
Table 1. Physicochemical properties of unsymmetrical esters of adipic acid.

| Ester  | Molecular Weight | Acid Number, mg KOH/g | Ester Number, mg KOH/g | d^20_4  |
|-------|-----------------|-----------------------|------------------------|---------|
| BBEA  | 302             | 0.1                   | 369                    | 1.0452  |
| HBEA  | 330             | 0.1                   | 337                    | 1.0636  |
| OBEA  | 358             | 0.1                   | 311                    | 1.0819  |
| DBEA  | 386             | 0.1                   | 288                    | 1.1003  |

3.1. IR spectra

The spectra of the synthesized esters lack an absorption band in the range of 1685-1687 cm\(^{-1}\), which is characteristic of stretching vibrations of the carbonyl group in associates of aliphatic carboxylic acids. The spectra of the synthesized adipates, the stretching vibrations of the carbonyl group are shifted to the high-frequency region and appear as a strong characteristic band in the region of 1737 cm\(^{-1}\). There are also absorption bands corresponding to the vibrations of the C–O–C fragment: 1176 cm\(^{-1}\) for butyl butoxyethyl adipate, 1175 cm\(^{-1}\) for hexyl butoxyethyl adipate, 1173 cm\(^{-1}\) for octyl butoxyethyl adipate, 1173 cm\(^{-1}\) for decyl butoxyethyl adipate.

3.2. Fungal resistance of alkyl butoxyethyl adipates

Table 2 shows the results of studies of the obtained alkyl butoxyethyl adipates for fungal resistance.

Table 2. Fungal resistance of alkyl butoxyethyl adipates.

| Ester  | Aspergillus niger | Pénicillium funiculosum | Trichoderma lignorum |
|-------|-------------------|-------------------------|----------------------|
| BBEA  | 4                 | 4                       | 4                    |
| HBEA  | 4                 | 4                       | 4                    |
| OBEA  | 3                 | 3                       | 3                    |
| DBEA  | 3                 | 3                       | 3                    |

The following strains of microscopic fungi were used as test organisms: *Aspergillus niger*, *Pénicillium funiculosum*, *Trichoderma lignorum*.

The growth and development of the mycelium of molds is possible only on nutrients. On all samples during the experiment time (28 days) there was a significant overgrowth of fungal mycelium. However, the mushroom resistance of octyl butoxyethyl adipate and decyl butoxyethyl adipate esters is slightly higher. Thus, the fungus resistance tests carried out have shown that the synthesized adipates are capable of serving as a food source for microscopic fungi.

3.3. Biodegradation of alkyl butoxyethyl adipates in soil

Biodegradation of the synthesized esters was tested in soil (figures 1-2). The study of the biodegradation of alkylbutoxyethyl adipinates showed that the mechanism of decomposition includes the sequential hydrolysis of ester bonds through the formation of a monoester of adipic acid. The initial esters under the conditions of natural destruction are rapidly hydrolyzed, since the reactivity of both carboxyl groups of adipic acid is the same.

The amount of monoester did not increase significantly, which confirms the instability of these metabolites. The study of the stability of the resulting metabolites is important, since it is believed that it is the monoester of the commercial plasticizer DEHP that exhibits toxicity and endocrine activity [14–18].

In the process of decomposition, a gradual accumulation of the corresponding alcohols is observed; however, butoxyethanol is completely biodegradable within four days, and the corresponding aliphatic
alcohols within 5–10 days, depending on the length of the hydrocarbon chain, are rapidly further attacked by microorganisms with the formation of the corresponding acids.

The mechanism of biodegradation of all obtained adipates is similar and proceeds with the formation of the corresponding alcohols and acids.

Adipic acid, butoxyethanol, and the corresponding aliphatic alcohols: Butanol, hexanol, octanol, and decanol were found as further products determined during the study. The resulting butoxyethanol also continues to undergo biodegradation with the formation of butanol and formic acid as metabolites.

With the lengthening of the chain of the alcohol being formed, the rate of hydrolysis during biodegradation decreases: decanol was formed most slowly in the system. The lengthening of the chain of the ether molecule limits the rate of degradation, that is, the shorter molecules are more actively processed by the organisms present in the soil.

Thus, the disposal of the developed plasticizers in the soil does not result in the formation of toxic substances, which confirms their ecotoxicological safety.

4. Conclusion
The study of the possibility of biogradation of the obtained esters of adipic acid showed that alkyl butoxyethyl adipates are characterized by a reduced resistance to fungi and, under environmental conditions, contribute to the biodegradation of the PVC composite. The study of the chemistry of biodegradation of the developed asymmetric adipates confirmed the environmental safety of these additives when used and in the process of disposal.
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