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Biodegradation of acetyl cellulose etrols

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Abstract. This work aimed to study the biodegradation dynamics of plasticized cellulose acetate samples (etrols) with different content of plasticizers. Isophthalic acid dimethyl ester and orthophosphoric acid tributyl ester were used as plasticizers. The targets of the study also included assessing the effect of the plasticizers' content on the degradation rate. The biodegradability of plasticized cellulose acetate samples was assessed by measuring the weight loss after exposure to active soil. For the experiment, an active soil of the following composition was prepared: garden soil - 89 vol. %, distilled water - 10 vol. %, microbiological preparation "Tamir" - 1 vol. %. All etrols samples showed a tendency to decomposition in active soil. The rate of sample degradation varied significantly. The highest degradation rate in active soil was shown by a sample containing 16 wt. % tributyl phosphate and 22 wt. % dimethyl isophthalate, as good as etrols sample containing 8 wt. % tributyl phosphate and 14 wt. % dimethyl isophthalate. The expected decomposition time of these samples in the active soil for 90% is 599 and 732 days, respectively. Changing of dimethyl isophthalate content did not affect the degradation rate. Withal the content of tributyl phosphate in the etrols induced a significant effect on the samples' weight loss. The consequence of the plasticizers' content on the weight loss rate for 145 days of exposure in the active soil is described by the equation $y = -4.76 + 1.25 \cdot Z_1 + 1.49 \cdot Z_2 - 0.04 \cdot Z_1^2 - 0.086 \cdot Z_2^2 + 0.000141$ where Z_1 is the content of dimethyl isophthalate, Z_2 is the content of tributyl phosphate.

1. Introduction

A large number of publications are devoted to the biodegradation rate of polymers and materials based on them. These questions concern the achievement of two opposite values of the biodegradation degree. Several polymeric materials (fibers, fabrics, artificial leather) require increased biostability. Most unutilized polymer waste demands a minimum biostability. For many materials, it is the demand to regulate the biodegradability at the time of use while maintaining the physical and mechanical properties under the influence of microorganisms, moisture, UV radiation.

The problem with the creation of polymeric materials with a given degradation rate is the lack of broadly accepted methods for determining this indicator. A mass of factors affects the degradation of polymers [1-7]. Many researchers use moisture and UV radiation methods to assess the degradation of polymers [8-12].

The legislation of many countries is expanding the requirements for the polymer waste biodegradability. The number of studies to determine the regularities of the influence of polymeric materials chemical structure and composition on their biostability is increasing. In the review by A.A. Popova, A.K. Zykova, E.E. Mastalygina [13] analyzed the influence of various factors on imparting biodegradability to polyolefins. These factors include the chemical structure of monomer units and the branching of polymer macromolecules.



Undoubtedly, materials based on natural polymers have a higher potential for biodegradation compared to synthetic polymers. However, the biodegradation rate depends not only on the polymer chemical structure but also on the chemical structure of the additives [14, 15]. In this case, the effect of plasticizers on the biostability of polymeric materials can have a synergistic effect. Materials based on natural polymers attract more and more attention from researchers in connection with the annual renewability of raw materials for their production [16-18]. The most common natural polymer is cellulose [19].

Materials based on cellulose ethers - etrols - are widely and broadly used in the manufacture. The biodegradability of etrols with cellulose acetates is well studied for materials based on cellulose diacetate [14, 20-22]. The biodegradation rate of etrols based on cellulose diacetate is significantly influenced by the plasticizers' chemical structure.

This work aimed to study the biodegradation in active soil of etrols based on cellulose triacetate and two plasticizers of various chemical structures widely used in industry: tributyl phosphate (TBP) and dimethyl isophthalate (DMI).

2. Materials and methods

Industrial samples of cellulose triacetate, tributyl phosphate, dimethyl isophthalate, and technical stearic acid (as a lubricant) were used as raw materials for the production etrols.

Etrol samples were prepared as follows. The components taken following the recipe (Table 1) were mixed in a laboratory mill at a frequency of 3000 rpm for 10 minutes, after which the resulting mixture was sent to a twin-screw laboratory extruder. Extrusion proceeded at a temperature of 170 ° C. The resulting extract was granulated, after which plates 5 mm thick were made from it by hot pressing. Rectangular samples with dimensions of 15 × 10 × 4 mm were cut from the obtained plates to assess the biodegradation of etrols.

Table 1. Composition of etrols

№	Component content, %			
	Cellulose acetate	DMI	TBP	Stearic acid
1	61.5	22	16	0.5
2	77.5	22	0	0.5
3	77.5	14	8	0.5
4	77.5	6	16	0.5
5	69.5	22	8	0.5
6	85.5	6	8	0.5
7	85.5	14	0	0.5
8	93.5	6	0	0.5
9	69.5	14	16	0.5

The etrols biodegradation was estimated by the weight loss value after their exposure to the active soil. For the experiment, an active soil of the following composition was prepared: garden soil (state standard 53381-2009) - 89 vol. %, distilled water - 10 vol. %, microbiological preparation "Tamir" (technical conditions 9291-002-70213832-2007) - 1 vol. %. The "Tamir" preparation contains the bacteria *Lactobacillus casei*, *Streptococcus lactis*, *Saccharomyces cerevisiae*, as well as saprophytic microorganisms, enzymes, and other biologically active substances that promote the decomposition of organic compounds [24]. The microorganisms that make up the preparation are not virulent, non-toxic, and are not pathogens. Preparation "Tamir" belongs to the IV class of hazard (low-hazard substances).

Before the experiment, the active soil was infused at room temperature for 21 days. During the study, the soil moisture was 30 wt. %. Before exposure to soil, etrol samples were dried in a drying cabinet at a temperature of 105 ° C to constant weight, and then immersed in the active soil to a depth

of 2 cm. After certain time intervals, the etrol samples removed from the soil, thoroughly cleaned and washed with ethyl alcohol, and then dried to constant weight.

3. Result and discussion

The dynamics of weight loss of etrols samples, when exposed to active soil, are shown in Figures 1 and 2. All obtained etrols are prone to decomposition in active soil; however, the rate of the decomposition process differs significantly. Samples 1 and 3 showed the most comprehensive tendency for biodegradation in soil. Linear regression equations describing the weight loss dynamics during exposure to active soil were found for each sample. These equations with the corresponding coefficients of determination characterizing the accuracy of the experimental data description presented in Table 2. Based on the obtained regression equations, a forecast was made about the time required for the degradation of etrols by 90%. The forecast results are also presented in Table 2.

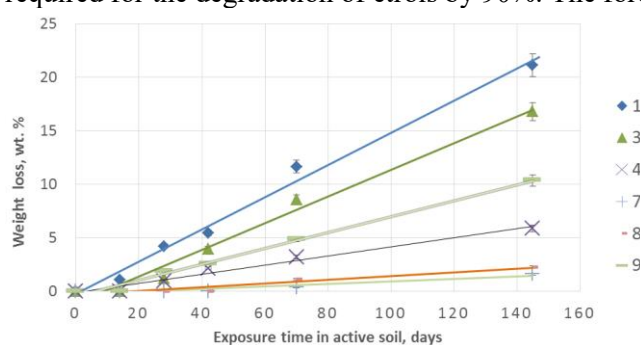


Figure 1. Dependence of weight loss by etrols samples (numbers of experiments in table 1) on exposure time in active soil.

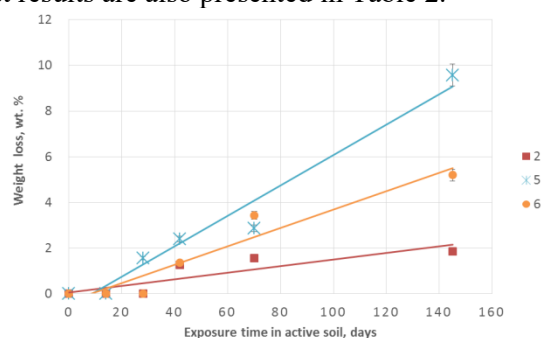


Figure 2. Dependence of the weight loss of etrol samples (numbers of experiments in table 1) on the exposure time in the active soil.

The expected degradation time for 90% of samples 1 and 3 is 599 and 732 days, respectively. This is an excellent indicator in comparison with the decomposition time of most synthetic polymeric materials. Etrol sample No. 1 contains 16 wt. % tributyl phosphate and 22 wt. % dimethyl isophthalate (the maximum content of plasticizers in the experiment) and has properties closest to commercially available large-tonnage thermoplastics. Etrol sample No. 3 contains 8 wt. % tributyl phosphate and 14 wt. % of dimethyl isophthalate and indicators of its rigidity and strength characteristics significantly exceed synthetic large-tonnage analogs (ultimate strength in bending - 47.9 MPa, Brinell hardness - 199 MPa, modulus of elasticity in compression - 2869 MPa).

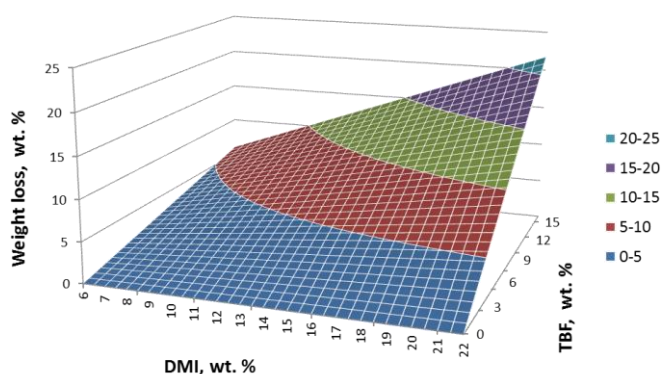
The content of plasticizers in the material not only correlates with the values of their physical and mechanical properties [24] but also significantly affects the biodegradability of etrols. To assess the effect of the content of dimethyl isophthalate (Z_1 , wt%) and tributyl phosphate (Z_2 , wt%) in the composition on their weight loss during exposure to active soil (Y , wt%) regression analysis of the experimental data was performed. The composition of the components of etrols, presented in Table 1, has good characteristics for statistical data analysis [25]. Using the Statgraphics Centurion XV program [26], the following adequate regression equation was obtained for a confidence level of 0.95:

$$Y = 0.062 \cdot Z_1 \cdot Z_2 \quad (1)$$

The graphical form of this dependence, shown in Figure 3, clearly shows the positive synergistic effect of the content of the plasticizer in etrol on their weight loss during exposure to active soil for 145 days.

Table 2. Regression equations describing the dynamics of etrol samples biodegradation

No.	Equation	Determina-tion coefficient R^2	The holding time required to achieve the degree of decomposition of 90% (forecast), days
1	$y = 0.1507x - 0.2472$	0.9899	599
2	$y = 0.0143x + 0.0657$	0.7407	6289
3	$y = 0.1245x - 1.1053$	0.9816	732
4	$y = 0.0427x - 0.0967$	0.9748	2110
5	$y = 0.0665x - 0.5808$	0.9639	1362
6	$y = 0.0402x - 0.3367$	0.9255	2247
7	$y = 0.0117x - 0.2528$	0.9038	7714
8	$y = 0.0174x - 0.3007$	0.9208	5190
9	$y = 0.0744x - 0.4075$	0.9916	1215

**Figure 3.** Dependence of etrols weight loss for 145 days of exposure in active soil on the content of plasticizers.

Figures 4, 5 show the most dynamically decomposing etrols samples surface photographs after 140 days of exposure in the active soil at 60X magnification. The surfaces of etrols samples No. 1 and No. 3 after exposure to active soil were significantly degraded, lost their smoothness and glossy shine, and became dull. Sufficiently deep furrows and pores appeared on them. The degradation of the surface promotes the processes of water absorption taking place in the moist environment of the active soil, which, in turn, are promoters of the microbiological effect on the material of etrol. Based on this, it can be assumed that in the future the process of etrols biodegradation will proceed with increasing acceleration.



Figure 4. Photo of the surface of etrol sample No. 1 after 140 days of exposure in active soil at 60X magnification.

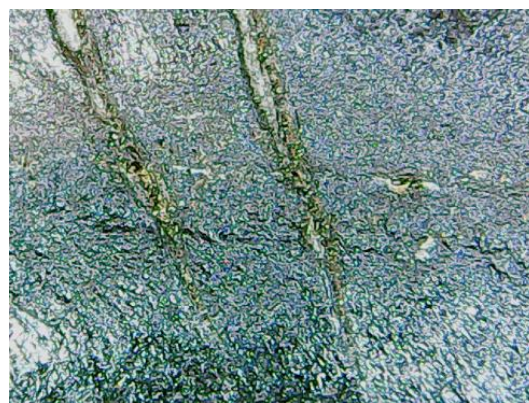


Figure 5. Photo of the surface of etrol sample No. 3 after 140 days of exposure in active soil at 60X magnification.

4. Conclusion

The result of this study is to determine the effect of the composition of etrols based on cellulose triacetate on the dynamics of their biodegradation in active soil. At the same time, a positive synergistic effect of plasticizers dimethyl isophthalate and tributyl phosphate on the weight loss of biodegradation of etrols for 145 days was established. The expected biodegradation time of 90% of the most dynamically biodegradable etrol is 20 months.

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