Determination of the degree of toxicity of EVA and Tedlar polymers during the disposal of components of crystalline solar panels

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Abstract. The article is devoted to the determination of the degree of toxicity of the polymer components EVA (ethyl vinyl acetate) and Tedlar® (polyvinyl fluoride) solar panels at the end of their useful life. A biotest analysis was chosen as a research method. The article discusses the main provisions of the selected method, as well as the advantages of the selected test organism. The article reflects the main provisions of the selected method. The results of a study to determine the toxicity of polymer components are also presented. Based on the data obtained, the dependences of the toxicity of compounds on time are constructed. These studies show the possible consequences of the interaction of the aquatic environment (rains) with the components of solar panels during their utilization (disposal).

1 Introduction

In recent decades, the global solar energy industry is developing rapidly, solar power plants have been becoming part of the energy infrastructure of many countries. Each year, new solar panels are installed which global power is growing exponentially. But along with the high environmental friendliness of the energy received, it is necessary to think about what will happen to these solar panels after the end of their warranty period which the average rating is 25-30 years. According to various agencies (IEA PVPS and IRENA), by 2050 the amount of solar panel waste will be 78 million tons [1].

85% of all solar panels currently produced are crystalline solar panels. On average, 0.5% degradation of this panel type occurs per year for various reasons, such as exposure to ultraviolet rays and moisture, the destruction of the film of ethyl vinyl acetate, etc [2].

In addition to the main photovoltaic unit and glass, the composition of crystalline solar panels includes polymeric materials EVA (ethyl vinyl acetate) and Tedlar® (polyvinyl fluoride), which the toxicity and chemical inertness have not yet been studied. Therefore, the burial of solar panels is undesirable, since the elements in question affect the environment, thereby endangering the health of the population. As a result, in July 2012, the European Union officially revised the Waste Electrical and Electronic Equipment (WEEE) Directive, adding that photovoltaic solar cells now must be included in the electronic waste management system and must be collected and disposed of.

2 General information about biotesting

A biotest analysis was chosen as a method for determining the degree of toxicity of EVA and Tedlar® polymeric materials, as the one of the main methods for detecting environmental toxicity using test objects that shows danger, regardless of which substances and in what combinations changes in vital functions were caused test - organisms.

For biotesting we can use different test objects. In this study, Paramecium caudatum was chosen as a test object, Ciliates have the most complex structure, combine the signs of a eukaryotic cell and the whole organism (able to respond to a stimulus with a complex of biological, physiological and biochemical changes, have pronounced taxis and are highly sensitive to toxicants of various nature. Paramecium caudatum in their biochemical parameters are very close to higher animals and humans, which makes it possible to extrapolate data obtained in biotesting using ciliates per person [3-6].

3 The essence of the chemotactic method of biotesting

The method for determining the toxicity of samples is based on the ability of test objects to respond to the presence of substances that are dangerous for their life activity in samples and to move directionally along the concentration gradient (in the direction of changing concentrations) of these substances (chemotactic reaction), avoiding their harmful effects [6].
If the test sample does not contain toxic substances, in the cuvette there will be a concentration of ciliates in the upper zone. The presence of toxic substances in the test sample leads to a different character of the redistribution of ciliates in the cuvette, namely: the higher the toxicity of the sample, the smaller the proportion of ciliates moves to the upper zone (the test sample). The biotest chemotactic technique is presented in Figure 1 [3].

![Fig. 1. Biotest chemotactic technique: 1 - harmless sample; 2,3 - sample of moderate toxicity; 4 - toxic test.](image)

The toxic effect is a significant difference in the number of ciliates cells observed in the upper zone of the cuvette in the sample containing no toxic substances (control), compared with this indicator observed in the test sample (experiment).

A quantitative assessment of the test - reaction parameter characterizing the toxic effect is made by calculating the ratio of the number of ciliates cells observed in the control and the studied samples, and is expressed as a dimensionless quantity - the toxicity index (T) [8].

4 Research

In the work, biotest analysis was carried out in accordance with Federal Environmental Regulatory Documents (ERD F) 16.3.16-10 "Methodology for determining the toxicity of production and consumption waste by the express method using the BIOTESTER series instrument", because the test samples are chemical polymer substances of complex composition.

To study the degree of toxicity of EVA and Tedlar® polymers, the mechanical dismantling of the solar panel was carried out, as a result of which the studied components were separated from the glass and the main photovoltaic unit. The obtained samples (weighing 2 grams each) of the studied components were mixed with distilled water (volume 50 ml), after which the resulting solution was mixed for several hours on the apparatus for shaking the liquid.

The concentration of ciliates in the cuvette was measured using the BIOTESTER 2M instrument, developed at the Department of Environmental Engineering at St. Petersburg Electrotechnical University "LETI". The device is intended to measure the spectral transmittance caused by moving microorganisms. The principle of operation is based on the natural features of ciliates moving up. (If the medium is not toxic, then a large number of individuals will emerge; if there is a toxicant, so the more the substance is toxic, then the smaller the number of ciliates will come up). Each of the test samples was analyzed in 3 cuvettes, 10 readings of the BIOTESTER-2M instrument were taken from each cuvette.

According to ERD F 16.3.16-10, to prevent gross errors during the analysis, the acceptability of the control sample was promptly evaluated according to the following inequality:

$$|I_{k_{\text{max}}} - I_{k_{\text{min}}}| \leq 0.2 I_{av,k},$$

where $I_{k_{\text{max}}}$ - maximum readings of the device for control samples, $I_{k_{\text{min}}}$ - minimum readings of the device for control samples, $I_{av,k}$ - average readings of the device for control samples [7].

4.1 Determination of the toxicity index of the test samples

Assessment of the toxicity of the sample was carried out by the relative difference in the number of ciliates in the upper zone of the cuvette in the control and analyzed sample. In accordance with PND F T 16.3.16-10 the toxicity index is calculated by the formula:

$$T = \frac{|I_{av,c} - I_{av,s}|}{I_{av,c}} \cdot K,$$

where $I_{av,c}$ – average readings of the device for control samples, $I_{av,s}$ – average readings for the test samples, $K$ – coefficient of dilution of the sample (factor).

The toxicity index T is a dimensionless quantity and can take values from 0 to 1 in accordance with the degree of toxicity of the analyzed sample.

According to ERD F 16.3.16-10, depending on the value of the index, samples are classified according to their toxicity into 3 groups:

I. Acceptable toxicity (0.00 < T ≤ 0.40).
II. Moderate toxicity (0.40 < T ≤ 0.70).
III. High degree of toxicity (T > 0.70).

When the toxicity index takes a value close to 1, then such a study cannot unambiguously characterize the true level of toxicity of the sample. Then, the test sample should be diluted with distilled water or Lozin-Lozinsky medium so that the value of T does not reach 1, and the resulting new index value is smart for the dilution coefficient. The sample is considered non-toxic, under the condition $T \leq 0.40$ [7].

The toxicity indices obtained as a result of mixing the solution with the test samples for 2 hours on the apparatus for shaking the liquid are presented in Figure 2.
The final values of the toxicity indices of the studied components are presented in table 1.

| The determined indicator | Analysis results | Toxicity index (excluding dilution ratio) | The degree of toxicity of the sample, T |
|---------------------------|------------------|------------------------------------------|----------------------------------------|
| Toxicity of the sample at the ciliates Paramecium caudatum | EVA 1 | 0.012±0.001 | Acceptable, $T = 0.012±0.001$ |
| Tedlar | 1 | 0.029±0.002 | Acceptable, $T = 0.029±0.002$ |

To study toxicity in detail we use Paramecium caudatum, a series of experiments were carried out to determine the dependence of the change in the degree of toxicity on the dissolution time of the components. The following time intervals were considered as control time points: 24 hours, 48 hours, 96 hours and 7 days (168 hours) - as the most used time intervals in methods for determining the toxicity of the environment using infusoria [9-12]. The results of the study are summarized in table 2.

| The determined indicator | Analysis results | Toxicity index (excluding dilution ratio) | The degree of toxicity of the sample, T |
|---------------------------|------------------|------------------------------------------|----------------------------------------|
| Toxicity of the sample at the ciliates Paramecium caudatum | EVA | 24 1 | 0.021±0.001 | $T = 0.021±0.001$ |
| Tedlar® | 24 1 | 0.023±0.002 | $T = 0.032±0.002$ |
| | 48 1 | 0.043±0.003 | $T = 0.043±0.003$ |
| | 96 1 | 0.054±0.004 | $T = 0.054±0.004$ |
| | 16 8 | 0.122±0.009 | $T = 0.122±0.009$ |
| | 48 1 | 0.041±0.003 | $T = 0.041±0.003$ |
| | 96 1 | 0.062±0.004 | $T = 0.062±0.004$ |
| | 16 8 | 0.144±0.010 | $T = 0.144±0.010$ |

As seen from the graphs, the toxicity indices increase if the polymer components are in significant time in solution, thereby approaching the value that characterizes the toxic environment.

5 Conclusion

In the course of the work, it was found that the toxicity indices of the EVA and Tedlar® components increase with prolonged exposure to materials in aqueous solution, approaching values characterizing an unsafe degree of toxicity to the environment and human health. Graphs are plotted reflecting the obtained dependence. These studies show the need to develop a methodology for the disposal of components of solar panels that prevent possible negative consequences for the environment and human health. Further research is planned to identify a more accurate dependence of the change in the degree of toxicity on time, as well as to determine the time interval when the dependence passes into a horizontal line (plateau).

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