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# Microbial degradation of polyetherguanidinacrylates

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Film-forming polyguanidinacrylates of a three-dimensional structure are synthesized by the interaction of oligoepoxide with guanidine and methacrylic acid or by the reaction of an oligoether with terminal guanidine fragments with urethane prepolymer and ethylene glycol methacrylic ether, followed by UV-initiated polymerization. According to the results of IR spectroscopy and thermograviometric analysis, the biodegradation of polymer materials occurs on the surface of these polymers without changing the internal chemical structure. The tensile strength and elongation of polyacrylates after the action of hydrocarbon-oxydizing bacteria do not change significantly, which indicates the stability of polymers and the possibility of their use as insulating coatings. In the presence of polyetheracrylate, the catalase activity of bacteria increased in 1.9–2.5Ntimes, and in the presence of polyether urethane acrylate, it decreased by 1.7 times. The studied materials stimulated the lipolytic activity of bacteria by 1.3–3.7 times and did not inhibit the growth of bacteria and their metabolic activity. An assessment of the biodegradation degree of the materials under the bacteria exposure showed that polyetheracrylate has the greatest degradation in the range of 3.1–3.6 %, for polyether urethane acrylate the degree was decreased by 2.6 times compared with control.

**Keywords**: polyguanidine acrylates, IR spectroscopy, thermogravimetry, biodegradation.

**Мікробна деградація поліетергуанідинакрилатів**. *М.Я.Вортман, Ж.П.Коптєва, Г.Є.Коптєва, Д.Р.Абдуліна, Г.О.Іутинська, В.М.Лемешко, В.В.Шевченко*

Плівкотвірні полігуанідинакрилати трьохмірної будови синтезовані взаємодією олігоепоксиду з гуанідином та метакриловою кислотою або по реакції олігоетеру з кінцевими гуанідиновими фрагментами з уретановим форполімером та метакриловим етером етиленгліколю з подальшою УФ-ініційованою полімеризацією. За результатами даних ІЧ-спектроскопії та термогравіометричного аналізу біодеградація полімерних матеріалів проходить на поверхні цих полімерів без зміни внутрішньої хімічної структури. Міцність до розриву та відносне подовження поліакрилатів після дії вуглеводеньокислювальних бактерій суттєво не змінюються, що свідчить про стійкість полімерів та можливе їх використання як ізоляційних покриттів. За присутності поліетеракрилату каталазна активність бактерій зростала в 1,9–2,5 рази, а для поліетеруретанакрилату — знижувалась у 1,7 рази. Досліджені матеріали стимулювали ліполітичну активність бактерій у 1,3–3,7 рази та не пригнічували ріст і метаболічну активність бактерій. Оцінка ступеню біодеструкції матеріалів за впливу бактерій показала, що найбільшої деградації зазнав поліетеракрилат, процент деструкції якого складав 3.1–3.6 %, для поліетеруретанакрилату цей показник знижується в 2,6 рази.

## 1. Introduction

The problem of biodeterioration of materials covers a wide range of scientific and practical cases related to the protection both in long-term storage conditions, and during the production, transportation and operation of raw materials and goods, from being damaged by microorganisms, in particular bacteria and micromycetes [1, 2]. The main goal of protective materials is to form a barrier layer preventing the development of corrosion and destruction of the metal surface, as well as limiting or completely preventing the formation of decomposition and corrosion products at the metal-coating interface [3]. To do this, the material of the protective coating for metals, first of all, must be biostable, have low permeability to water, gases, chloride and sulfate ions, have sufficient adhesion to the metal, mechanical strength and structural stability [2].

One of the reasons for a decrease in the properties of protective materials is the metabolic activity of microorganisms that can initiate or stimulate destruction processes. In the vast majority of cases, for the biodegradation process, the material must contain functional groups capable of hydrolysis [4–9]. The following groups are capable of hydrolysis: ester, carbonate, amide, anhydride, urethane, urea, semicarbazide groups, which are similar to ester and peptide (amide) groups, that are part of many natural low-molecular substances and polymers-lipids, peptides, proteins. The molecular structure of the polymer has a significant impact on the hydrolysis process, and the initial hydrolysis rate is higher for lower-molecular polymers [1, 2]. As a result, materials exposed to microbial attack reduce the economic value and the service life of products is disrupted.

Anticorrosive protection of various surfaces is provided by insulation coatings, which today are diverse in chemical structure. The most resistant to the action of microorganisms are high-molecular polymers: polyethylene, polyurethane, polystyrene, polyvinyl chloride [1]. There are carbon-chain polymers, — polyethylene, polypropylene, polyvinyl chloride, etc. and hetero-chain polymers, which are based on oxygen and nitrogen atoms (polyamide, polyurethane) in addition to carbon. However, they are exposed to microorganisms, in particular hydrocarbon-oxidizing, denitrifying bacteria as: *Acinetobacter*, *Alcaligenes*, *Arthrobacter*, *Burkholderia*, *Brevibacterium*, *Corynebacterium*, *Micrococcus*, *Mycobacterium*, *Nocardia*, *Pseudomonas*, *Rhodococcus*, *Serratia*, *Bacillus* [10, 11].

In the process of degradation, due to mechanical destruction (formation of biofilms, fouling, germination of mycelium), microbial enzymes destroy complex polymers, resulting in the formation of short-chain molecules, for example, oligomers, dimers and monomers that are smaller in size, have altered properties (water-soluble), are able to pass through external bacterial membranes, and then be used as sources of carbon and energy. This initial process of polymer degradation is called depolymerization. In general, the path of material degradation is often determined by environmental conditions and the adaptive potential of microorganisms [12–14].

One of the ways to increase the microbial resistance of coatings is the modification with biocidal substances that inhibit the growth and development of corrosive microorganisms. An effective method for increasing the biostability of bituminous coatings is their modification by products of industrial processing of coal and shale resins, which have high anticorrosive properties but contain carcinogenic compounds and therefore are limited in use [14].

The search for new promising materials that are resistant to the effect of microorganisms remains timely and relevant. Previously, we tested a number of polyurethane-based materials, and they turned out to be bio-resistant to the action of destructive bacteria. Physical and chemical quality indicators of perchlorovinyl-polyurethane enamel modified with a nanostructured oligomer, adhesive strength and tensile strength were at the level of the control variant [15].

This paper presents the results of our study of newly synthesized polyguanidine acrylates — polyester acrylate and polyether urethane acrylate; due to high adhesion to various surfaces, low shrinkage during curing, good electrical insulating properties, chemical resistance and high strength, they can be used to create various special-purpose materials in the production of UV-curable coatings for printing plates, microelectronic circuits, protective coatings. In the literature there are data on the biodegradation of segmented polyurethanes [16, 17] and polyurethane acrylates [18] and there are no data about the microbial biodegradation of polyguanidine acrylates. It is known that materials based on oligoether

acrylates and oligoether urethane acrylates have a unique set of valuable performance properties. High adhesion to various surfaces, low shrinkage during curing, good electrical insulation properties, chemical resistance and high strength determine their use in various fields of science and technology in the production of UV-cured coatings for printing plates, microelectronic circuits, protective coatings [16–19].

The aim of the work was to study chemical and physico-mechanical changes in newly synthesized materials — polyguanidine acrylates under the influence of test cultures of hydrocarbon-oxidizing bacteria.

## *2. Experimental*

**The following materials** were used: films of newly synthesized polyguanidine acrylates-polyether acrylates and polyether urethane acrylates, which were used to study the destruction under the action of hydrocarbon-oxydizing bacteria.

Aliphatic epoxy oligomers DEG-1 with a content of 0.6 %, hydroxylgroups and aromatic Dian oligomers DER-331 with a content of 0.3 %, hydroxyl groups, oligooxytetramethylene glycol (OTMG) MW 1000 were dehydrated by heating in vacuum for 2–6 hours at 80–90°C and a final pressure of 2 mm Hg. Guanidine hydrochloride (GD), toluylene diisocyanate (TDI) — a mixture of isomers 2,4 and 2,6 (Aldrich company, purity 99.9 %), alcohol of medical rectificate (96 %) were used without additional purification. Dimethylformamide (DMFA) was purified by distillation.

*Preparation of guanidine-containing polyether acrylate*. The reaction was carried out in two stages. At the first stage, a guanidine-containing oligoether with end epoxy groups was obtained. 1.90 g (0.02 mol) of guanidine hydrochloride, previously transferred from the salt form to the base form with alkali, was added to 9 g (0.03 mol) of DEG-1 MW 300 oligoepoxide. The reaction proceeded for 2 hours at 60°C in ethanol (solution concentration 60 %). Control over the completion of the reaction was carried out by a titrimetric method based on the content of epoxy groups in the final product. At the second stage, 1.72 g (0.02 moles) of methacrylic acid was added to 10.2 g (0.01 moles) of the resulting oligoether with end epoxy groups. The reaction proceeded for 2 hours at 60°C in ethanol (solution concentration 60 %) and in the presence of the catalyst triphenylphosphine. The completion of the reaction was controlled by IR spectroscopy, tracing the disappearance of the absorption band of epoxy groups at 920 $cm^{-1}$. The resulting product was polymerized by UV-initiated photopolymerization in the presence of benzophenone — 0.2 % by weight of the components. The degree of conversion to polymer was evaluated using a gel fraction, which was determined by extracting a polymer sample in a Soxhlet apparatus at 50°C in acetone for 6 hours.

**Preparation of guanidine-containing polyetherurethanacrylate**. The reaction proceeded in four stages. At the first stage, a urethane prepolymer was obtained. 3.46 g (0.02 moles) of toluylenediisocyanate was added to 10 g (0.01 moles) of oligooxytetramethylene glycol MW 1000. The reaction proceeded for 1 hour at 90°C. The completion of the reaction was controlled by a titrometric method based on the content of NCO groups. At the second stage, 1.12 g (0.01 moles) of ethylene glycol methacrylic ether was added to 13.46 g (0.01 moles) of urethane prepolymer. The reaction proceeded in bulk at room temperature in the presence of a catalyst — dibutyl tin dilaurate. The completion of the reaction was controlled by the titrimetric method based on the content of NCO groups. At the third stage, a guanidine-containing oligoether with terminal guanidine fragments was obtained. An alcoholic solution of guanidine 11.9 g (0.2 moles) obtained before the reaction was added to 36.5 g (0.1 moles) of the epoxy oligomer in a 70 % ethanol solution with constant stirring. Synthesis proceeded at 50–60°C for 2–3 hours. At the fourth stage, 2.43 g (0.005 moles) of a guanidine-containing oligoether with terminal guanidine fragments was added to 14.46 g (0.01 moles) of the product obtained at the second stage. The reaction proceeded at (60–70)°C for two hours in dimethylformamide. The solvent was selected in such a way that both the initial reagents and the final product were dissolved in it. The completion of the reaction was controlled by the titrometric method based on the disappearance of isocyanate groups, as well as by IR spectroscopy — based on the disappearance of the absorption band of isocyanate groups at 2300 $cm^{-1}$. Films of 100 μm were cast from a solution of the photopolymerized composition. The resulting product was polymerized by UV-initiated photopolymerization.

**The object of the study** was the process of microbial destruction of polymer materials based on polyetheracrylates. As testing

cultures, we used hydrocarbon-oxidizing bacteria (HOB) *Pseudomonas pseudoalcaligenes* 109, *Rhodococcus erythropolis* 102, *Bacillus subtilis* 138, which were isolated from damaged gas pipeline coatings and stored in the collection of the Department of General and Soil Microbiology of the D.K.Zabolotny Institute of Microbiology and Virology of the National Academy of Sciences of Ukraine. The effect of HOB on the test materials was studied at a temperature of 28±2°C in liquid Tauson nutrient medium, in which the test materials were the only source of carbon. Samples with sizes of 20×20×1 mm were weighed on an electronic balances (ANG-200, AXIS), sterilized in a 70 % ethanol solution (30 min), and with UV irradiation with a wavelength of 256 nm (15 min on each side), immersed in a sterile Tauson nutrient medium, which was inoculated with a liquid culture of the above bacterial strains in an amount of 5 % vol/vol. The exposure duration was 90 days. The number of bacteria in the culture liquid was determined by the tenfold limit dilutions method [19]. Control samples were placed separately in a sterile Tauson medium. After the exposure period, the samples were removed from the cultural liquid, washed several times with distilled water, dried at room temperature, and weighed. The destruction of the samples was expressed in % [20].

**Enzymatic studies**. The culture liquid was centrifuged for 20 minutes at 2000 g on a centrifuge with a 5810R rotor Eppendorf (Germany) to precipitate bacterial biomass; the supernatant liquid was used for research. The lipolytic activity was determined spectrophotometrically by reaction with *p*-nitrophenyl palmitate (PNFP); catalase activity was analyzed using 0.03 % hydrogen peroxide, which formed a stable colored complex with a 4 % molybdenortophosphate solution [21]. Protein was determined by the conventional Lowry method.

**Study of physicochemical and physicomechanical properties of materials**. Changes in the chemical composition of the studied materials were studied by infrared Fourier IR spectroscopy. The spectra were recorded by the method of total internal reflection using an attached ATR in the spectral region 400–4500 $cm^{-1}$ on a "TENSOR-37" spectrophotometer (Bruker Optik, Germany) [22]. The samples were examined as elastic films, and $^1H$ NMR spectra were captured on the "Varian VXR-400 MHz" device in $CDCl_3$. The thermophysical characteristics — glass transition temperature of polyguanidine acrylates were determined on a Q2000 device (TA Instruments, USA) in air in the temperature range of –90°C to 150°C at a heating rate of 20 deg/min. Changes in the mass of the samples as a function of temperature were studied by the thermograviametric method on a Q50 (thermogravimetry analyzer) ("TA Instruments", USA) in the temperature range from room temperature to 700°C at a heating rate of 20 deg/min in air. The method is based on a combination of differential thermal analysis with thermogravimetric analysis and examines the chemical and physicochemical processes occurring in a substance under conditions of temperature change [23]. The tensile strength and elongation of the newly synthesized materials were determined by generally accepted methods [15].

The repetition of experiments is threefold. Statistical processing was performed using OriginPro 2016 (ver. b 9.3.226. www.originlab.com).

## 3. Results and discussion

The scheme of synthesis of guanidine-containing oligoether acrylate with a linear structure and guanidine-containing oligoether urethane acrylate in which the chain extension is a guanidine-containing oligoether, can be represented as follows:

**A** — oligoether acrylate **B** — oligoether urethane acrylate

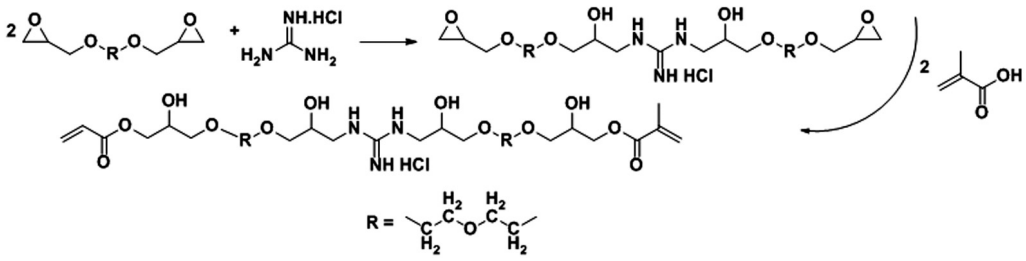
The structure of the obtained oligomers is confirmed by the data of IR spectroscopy (Fig. 1) and NMR spectroscopy (Fig. 2).

The IR spectrum of oligoether acrylate (νOH) 3400 $cm^{-1}$, (νNH) 3156 $cm^{-1}$, (ν$CH_3$) 2949 (νCH) 2896 $cm^{-1}$, (ν$CH_2$) 2868 $cm^{-1}$, 1648 $cm^{-1}$ (νC=N), (1120, 1250, 1320) $cm^{-1}$ (νC–O–C).

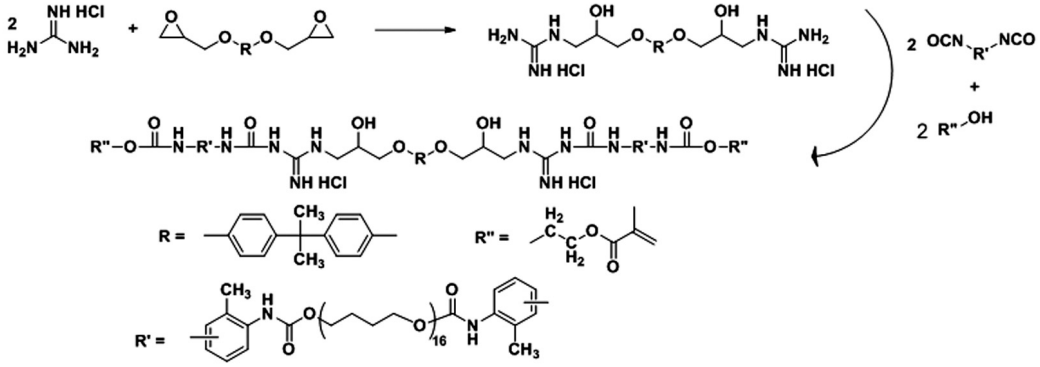
The IR spectrum of oligoether urethane acrylate (νOH) 3360 $cm^{-1}$, (νNH) 3120 $cm^{-1}$, (ν$CH_3$) 2960, (νCH) 2890 $cm^{-1}$, (ν$CH_2$) 2840 $cm^{-1}$, 1660 $cm^{-1}$ (νC=N), 1420, 1520 $cm^{-1}$ ($C_6H_4$), (1140, 1270, 1330) $cm^{-1}$ (νC–O–C).

$^1H$-NMR oligoether acrylate 2,45, ppm. –NH (NH–$CH_2$), 2.58 ppm. –$CH_2$ ($CH_2$CHOH, 3.58 ppm. –OH (CH–OH, 3.96 ppm. –CH (CH–OH), 6.5 ppm, 7.0 ppm. –NH groups.

$^1H$-NMR oligoether urethane acrylate 1.72 ppm. (т, 3H, –$CH_3$, 2.25 ppm. –NH (NH–$CH_2$), 2.58 ppm. –$CH_2$ ($CH_2$CHOH, 3.28 ppm. –OH (CH–OH, 3.56 ppm. –CH (CH–OH), 685 ppm. –CH benzene ring, 7.2 ppm and 7.8 ppm. –NH groups.



A - oligoetheracrylate



B- oligoetherurethanacrylate

On the basis of the obtained unsaturated guanidine-containing oligoguanidine acrylates, three-dimensional film-forming polymers were obtained by UV-initiated polymerization. The synthesized polyether methacrylate was characterized by the presence of a single glass transition temperature (365 K) and, accordingly, a homophasic structure. The gel fraction content is 96 %. Two glass transition temperatures (225 and 320 K) and, accordingly, a heterophase structure were present in polyether urethane acrylate. The gel fraction content is 98 %. The resulting polymers are soluble in dimethylformamide, dimethyl sulfoxide and insoluble in alcohols, ketones, and hydrocarbon solvents.

Studies of the effect of HOB test cultures on the biodegradation of the obtained polymeric materials showed that over 90 days of exposure, the number of hydrocarbon-oxidizing bacteria increased by 1–2 orders of magnitude, depending on bacterial strains and materials. In the presence of polyether acrylate, the number of bacteria was $10^7$–$10^8$ cells/ml, in the presence of polyetherurethane acrylate — $10^6$–$10^7$ cells/ml. In the control medium (without materials), the bacterial titer ranged from $10^5$ to $10^7$ cells/ml. There was also a change in the acidity of the nutrient medium. The initial pH of the Touson medium was 6.8. Bacteria not only grew, but also showed metabolic activity in the presence of the studied materials and when the pH of the medium changed to alkaline from 6.8 to 8.6. So, the studied materials did not inhibit the growth and metabolic activity of HOB.

It is known that microorganisms synthesize a number of enzymes that regulate chemical reactions occurring in bacterial cells, and these enzymes, as noted above, can also affect polymer materials. Depending on the degree of aggressiveness of the environment in which the materials are tested, that is, under the influence of microbiological and physicochemical factors, damage of the materials increases. The catalase and lipase activity of the HOB was measured (Fig. 4) to assess their impact on the newly synthesized materials.

The catalase activity of bacteria in the control (Tauson medium without materials inoculated by bacteria) was 0.14±0.03 4.4±0.6 U·mg$^{-1}$ protein. In the presence of polyether acrylate, the catalase activity of bacteria increased by 1.9–2.5 times; in the presence of polyetherurethane acrylate, it decreased by 1.7 times. The lipolytic activity of bacteria in the control was 2.6±0.5 — 9.7±1.1 U·mg$^{-1}$ protein. Compared to the control, the addition of polyether acrylate

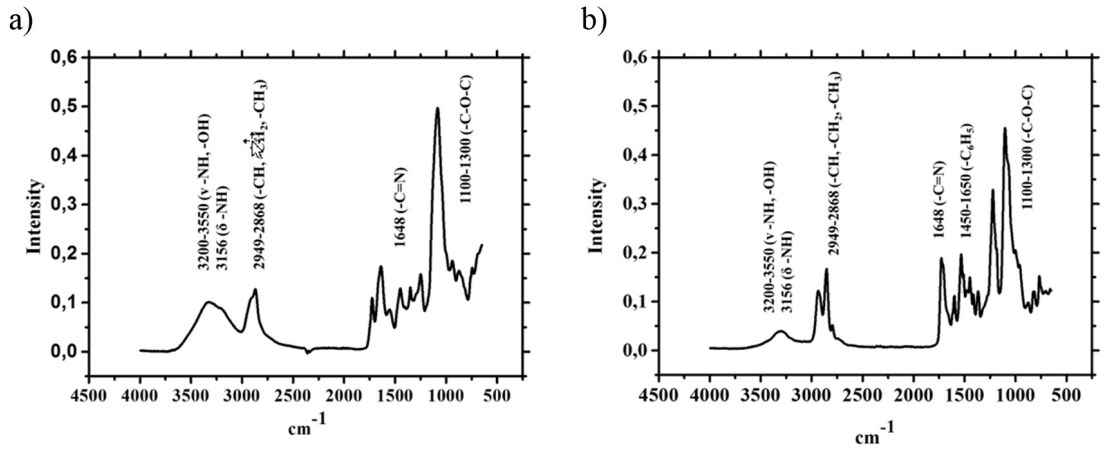



Fig. 1. IR spectra of guanidine-containing oligoether acrylate (A) and oligoether urethane acrylate (B).

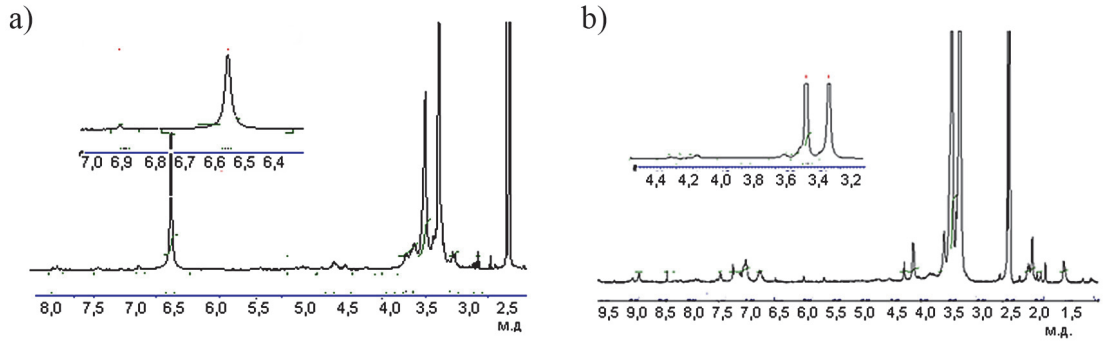



Fig. 2. $^{1}$H NMR spectra of guanidine-containing oligoether acrylate (A) and oligoether urethane acrylate (B).

and polyetherurethane acrylate to the nutrition medium stimulated the enzymatic activity of HOB by 2.5–3.7 and 1.3–3.0 times, respectively. Among the studied strains, high catalase and lipase activity was observed both in the experiment and in the control for *B. subtilis* 138 (Fig. 3).

Both changes in the metabolic and enzymatic activity of bacterial test-cultures were observed during the introduction into the materials. The degree of destruction of the studied materials under the influence of HOB was evaluated. An indicator of material degradation is the mass loss of samples of the materials affected by bacteria, which was used to calculate the percentage of destruction (Table 1).

According to Table 1, polyether acrylate was most degraded (3.1–3.6 %). In the control variant (material in the Tauson medium without bacteria), the destruction was 1.3 %. In the presence of other material — polyetherurethane acrylate, the destruction rate was lower (1.22–1.36 %), and in the control 1.05 %. Consequently, the introduction of the urethane component reduces the percentage of destruction of the new material in 2.3–3.0 times.

Changes in the structure of materials after the exposure to HOB cultures were determined by IR spectroscopy. Table 2 presents the main absorption bands of the IR spectra of samples of polyguanidine acrylates after the action of PSA after 90 days of the experiment. Both in the control samples of polyether acrylate, and in the IR spectra of samples affected by the bacterial test-cultures, absorption bands were present (νOH) 3400 $cm^{-1}$, (νNH) 3156 $cm^{-1}$, (ν$CH_3$) 2949 $cm^{-1}$, (νCH) 2896 $cm^{-1}$, (ν$CH_2$) 2868 (νC=N) 1648 $cm^{-1}$, (νC–O–C) 1100–1300 $cm^{-1}$ (Table 2). When exposed to bacteria, no changes in the absorption bands occurred after 90 days. In the control samples of polyetheru rethane ac rylate, and in the IR spectra of samples influenced by the testing cultures of bacteria, there were also

Table 1. Destruction of polymer materials under the action of HOB

| Bacterial strains | %, destruction | |
|---|---|---|
| | Polyetheracrylate | Polyetherurethanacrylate |
| *P. pseudoalcaligenes* 109 | 3.4±0.3 | 1.36±+0.1 |
| *R. erythropolis* 102 | 3.1±+0.2 | 1.35±+0.1 |
| *B. subtilis* 138 | 3.6±+0.5 | 1.22±+0.09 |
| Control | 1.3±+0.1 | 1.05±+0.1 |

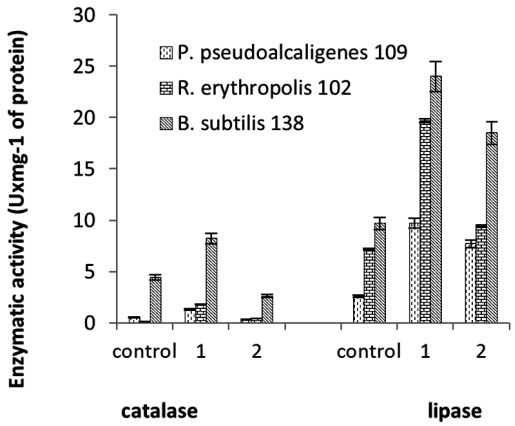



Fig. 3. Enzymatic activity of HOB in the presence of polymer materials: control — polymer — free nutritional medium; *1* — polyetheracrylate, *2* — polyetherpolyurethanacrylate.

absorption bands, like for polyether acrylate, but there was also a band of the benzene ring (ν $C_6H_5$) 1450–1650 $cm^{-1}$. With exposure to *R. erythropolis*102 and *B. subtilis* 138 after 90 days, there were no changes in the absorption bands.

Changes in the structure of the materials after the exposure to HOB test-cultures were also determined by thermograviometry analysis [24]. Fig. 4 shows thermograms of the decomposition of guanidine-containing polyether acrylates and polyetherurethane acrylates after the exposure to HOB during 90 days of the experiment. As we see from Fig. 4 and Table 3, the initial degradation temperature for guanidine-containing polyether acrylate does not decrease under influence of HOB, but under influence of *R. erythropolis* 102 and *B. subtilis* 138 it rises by 5–6°C. Analysis of the thermogram curves shows that the decomposition process occurred in the studied materials in four stages for polyether acrylate and in three stages for polyetherurethane acrylate. Four

Table 2. The main absorption bands of the IR spectra of polymeric materials

| Major Functiomal Group | Absorbtion Frequency Region, $cm^{-1}$ | |
|---|---|---|
| | Polyether acrylate | Polyether urethane acrylate |
| ν O–H | 3400 | 3360 |
| ν N–H | 3156 | 3120 |
| ν C–H | 2949 | 2960 |
| ν $CH_2$ | 2896 | 2890 |
| ν $CH_3$ | 2868 | 2840 |
| C=C aromatic | – | 1420, 1520 |
| ν C = N | 1648 | 1660 |
| ν C–O–C | 1120, 1250, 1320 | 1140, 1270, 1330 |
| δ:C–H | 760 | 780 |

and three peaks were observed on the decomposition thermograms, respectively. The initial decomposition temperature of guanidine-containing polyether acrylate after HOB exposure increased by 5–6°C (2 %) compared to the control. The first peak was observed at 160°C, the degree of decomposition was 8 %, and this process is associated with the destruction of low-molecular components and structural defects of the polymer. At 317°C (destruction temperature with sample mass loss of 50 %), the second peak of the decomposition of guanidine groups is observed, and the third peak is observed at 438–446°C and 588–600°C (destruction temperatures for sample mass loss of 70 % and 90 %, respectively).The decomposition process of polyetherurethane acrylate took place in three stages, as evidenced by the presence of three peaks on the thermogram curves. After the action of *P. pseudoalcaligenes* 109 and *R. erythropolis* 102, the initial decomposition temperature practically does not

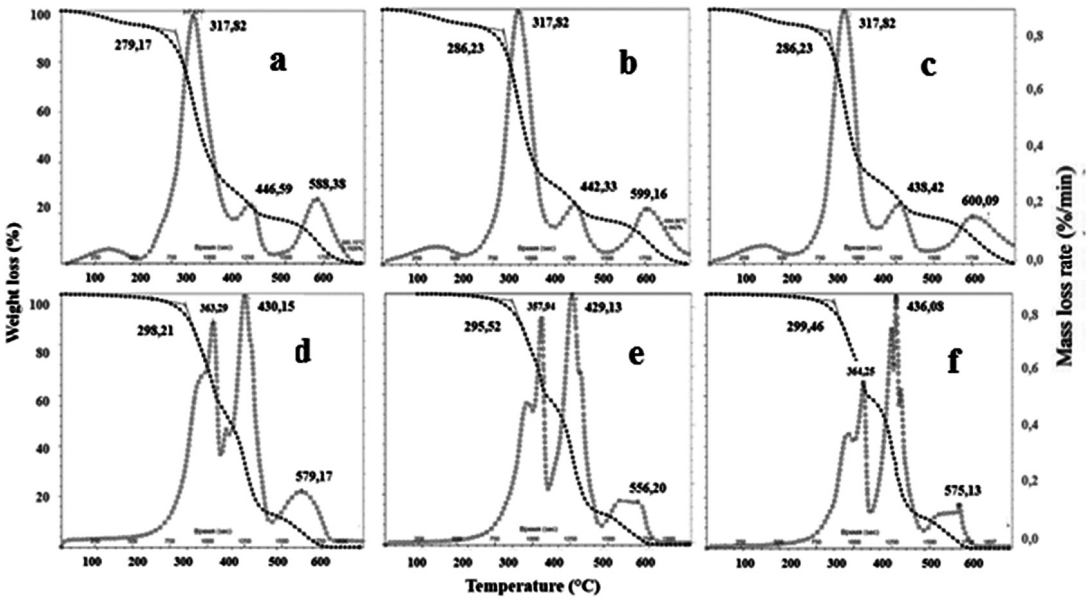



Fig. 4. Thermograms of samples of guanidine-containing polyether acrylates (a–c) and polyether urethane acrylates (d–f) after the exposure to HOB for 90 days; a, d — control, b, e — *R. erythropolis* 102. c, f — *B. subtilis* 138.

Table 3. Decomposition temperature of guanidine-containing polyether acrylate and polyether urethane acrylate after the exposure to HOB within 90 days of exposure

| Bacterial strains | Initial and degradation temperatures at % sample mass loss | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | Initial $T_d$, °C | 50.00 | 70.00 | 90.00 | Initial $T_d$, °C | 50.00 | 70.00 | 90.00 |
| | Polyether acrylate | | | | Polyether urethane acrylate | | | |
| *R. erythropolis 102* | 286.23 | 317.82 | 439.42 | 600.09 | 295.52 | 357.94 | 429.13 | 556.20 |
| *B. subtilis 138* | 286.23 | 317.82 | 436.33 | 599.16 | 299.46 | 364.25 | 436.08 | 575.13 |
| Control | 279.17 | 317.82 | 446.59 | 588.38 | 298.21 | 363.29 | 430.15 | 579.17 |

change as compared to the control. At 357–364°C (degradation temperature with sample mass loss of 50 %), there is a sharp peak associated with the decomposition of urethane groups. At 429–436°C and 556–575°C (degradation temperature for sample mass loss of 70 % and 90 %, respectively), deep processes occur associated with loosening and oxidation of the hydrocarbon skeleton of the polymer.

Since the initial decomposition temperature did not decrease for the two studied materials, and in some cases even increased, it can be assumed that the newly synthesized polymer materials did not lose their properties after exposure to HOB.

The study of the physical and mechanical properties of polyacrylates after the exposure to HOB (Table 4) showed that the tensile strength of the initial polyetheracrylate is 8 MPA, the elongation is 85 %. After the exposure to HOB, the physical and mechanical parameters practically did not change. For the initial polyetherurethane acrylate, the tensile strength is 12 MPA, the elongation is 100 %. After the exposure to HOB, the physical and mechanical parameters did not change significantly for the two materials studied. We can conclude that the newly synthesized polymer materials did not lose their physical and mechanical properties after the exposure to HOB. The obtained data correlates with the data of IR spectroscopy and thermogravimetric analysis.

It is known that simple destruction of an object is observed when it is made of a material that is degradable in a biological environment. As for polymers, such materials should not have a spatial structure and

Table 4. Physical and mechanical properties of polyacrylates exposed to HOB

| Experiment variants | Tensile strength, MPA | Elongation, % | Tensile strength, MPA | Elongation, % |
|---|---|---|---|---|
| | Polyether acrylate | | Polyether urethane acrylate | |
| Initial | 8.0±0.2 | 85±0.9 | 12.0±0.3 | 100±1.9 |
| Control | 8.0±0.2 | 82±0.8 | 11.0±0.3 | 97±1.7 |
| *P. pseudoalcaligenes* 109 | 7.0±0.1 | 80±0.7 | 10.0±0.2 | 95±1.5 |
| *R. erythropolis* 102 | 6.5±0.1 | 82±0.8 | 11.0±0.3 | 93±1.2 |
| *B. subtilis* 138 | 7.0±0.1 | 79±0.7 | 10.0±0.1 | 95±1.5 |

must contain polar functional groups in the main chain or in the side branches, which ensure the solubility of the polymer in an aqueous medium.

In the vast majority of cases, for biodegradation, the main chain must contain functional groups capable of hydrolysis. The molecular structure of the polymer has a significant influence on the hydrolysis process, and the initial hydrolysis rate is higher for lower-molecular polymers [1, 2]. It is known that segmented polyurethanes are blockcopolymers (blockcopolyurethans) that have a rather complex structure and include two types of chain fragments — flexible blocks and "rigid" fragments containing aromatic or cycloaliphatic groups and groups that provide intermolecular hydrogen bonds (amide and urea). The mechanisms of hydrolysis of polyetherurethanes are similar to the mechanisms of hydrolysis of the corresponding low-molecular compounds. Thus, the decomposition of polymers can occur both due to chemical hydrolysis and the participation of enzyme systems. In this case, different resistance of polymers to (different) various enzymes was observed. Most of the polyurethanes currently used are simple polyurethanes, i.e. synthesized from polyol based on polyether. Simple polyurethane is rarely susceptible to microbial biodegradation [24–28].

The data obtained from the study of the bacterial action on the synthesized guanidine — containing polyether methacrylates and polyether urethane acrylates using IR spectroscopy and thermogravimetric analysis indicates that the oxidative processes do not occur in the studied materials; the initial decomposition temperature of polymer materials does not decrease, and in some cases even increases. The study of the physical and mechanical properties of polyacrylates exposed to HOB showed that the tensile strength and elongation do not change significantly. The obtained data correlates with the data of IR spectroscopy and thermogravimetric analysis. Based on the low values of the destruction coefficient of polymer materials, it can be assumed that under the action of these bacteria, a slight biodegradation occurs on the surface of these polymers.

The obtained results on the number of bacteria under the experimental conditions indicate that the studied materials do not inhibit bacterial growth and the bacteria are able to use them as the only source of carbon.

Determination of the degree of destruction of materials showed that polyether urethane acrylate is more resistant to bacterial attack, the percentage of destruction of which was insignificant. Polyester acrylate has experienced the greatest impact of hydrocarbon-oxydizing bacteria. It is known that polyurethanes as heterochain thermoplastic polymers are used in various fields of technology and are more resistant to the action of corrosive microorganisms than materials based on polyethylene, polyvinyl chloride and petroleum bitumen [17]. Therefore, the tested polyurethane-based material has potential for protecting various structures from bio-damage.

The enzymatic activity of bacteria depended on the strains and materials introduced into the Tauson medium as the only source of carbon. The catalase activity of the destructors of the polymer containing polyurethane was significantly lower (3.1–4.5 times) than in the presence of polyester acrylate.

It is known that the function of catalase is to break down toxic hydrogen peroxide, which is formed as a result of various oxidative processes in bacterial cells [29]. We previously showed that the introduction of guanidine-containing polyethylene oxide hydrogel into the Tauson medium as an additional source of carbon and energy led to a

decrease in the catalase and lipase activity of hydrocarbon-oxidizing bacteria. Under the influence of the studied bacteria, hydrogel destruction occurred up to 88.4 % of the initial value [30]. In addition, studying the effect of polymer materials on hydrocarbon-oxidizing bacteria, we proved that the presence of expanded polyethylene, ethylene vinyl acetate and rubber, as the only sources of carbon in the medium, contributed to a decrease in catalase activity in *R. erythropolis* 102 and *P. pseudoalcaligenes* 109 and lipase activity in *R. erythropolis* 102 and *B. subtilis* 138 [31].

According to microbiological parameters, the newly synthesized materials did not inhibit the growth and metabolic activity of bacteria. Also, the enzymatic activity of HOB, namely catalase, increased in the presence of polyetheracrylate, and in the presence of polyether urethane acrylate it decreased. On the contrary, the lipolytic activity of HOB increased in the presence of the test materials. However, minor changes in the structure and physical and mechanical properties of the studied compositions after the exposure to HOB indicate that the newly synthesized materials are resistant to the action of corrosive bacteria. It should be considered that one of the mechanisms of bio-damage to synthesized protective materials by corrosive bacteria is surface biodegradation in those areas of the surface where the most hydrophilic and disordered macromolecule particles are concentrated. Therefore, the resulting polymers can be used to create protective coatings.

## *4. Conclusions*

Film-forming materials polyguanidin acrylates were synthesized by the interaction of oligoepoxide with guanidine and methacrylic acid, or by the reaction of a guanidine oligoether containing terminal guanidine fragments with urethane prepolymer and ethylene glycol methacrylic ether, followed by UV-initiated polymerization.

According to the degree of biodegradation of the materials, polyether acrylate underwent the greatest microbial degradation, the percentage of destruction of which was 3.1–3.6 %. The introduction of the urethane component and the production of polyether urethane acrylate led to a decrease in the destruction of the material by 2.6 times.

The results of IR spectroscopy and thermogravimetric analysis in studying the action of bacteria on the synthesized guanidine-containing polyether methacrylate and polyether urethane methacrylate indicate that oxidative processes do not occur in the studied materials. The study of the physical and mechanical properties of polyacrylates after the effect of HOB showed that the tensile strength and elongation do not change significantly. Based on the low degradation coefficient of polymeric materials, it can be assumed that under the influence of these bacteria, insignificant biodegradation occurs on the surface of these film-forming polymeric materials.

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