

## Antibiocorrosive coatings based on antimicrobial polymer hybrid composites

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Antimicrobial composites and coatings with specific properties based on polyurethane and nano sized arsenic trioxide ( $As_2O_3$ ) obtained by transformation of secondary resources were created and studied. Thermo-physical characteristics, basic tribological (scratch resistance, wear, dynamic friction) and surface properties of the obtained composites and materials were studied. The addition of silicon-organic oligomers into polyurethane matrix modifies thermal, tribological and operational properties of corresponding materials in the desired direction. Strong intermolecular interactions and compatibility between materials components were verified by performed tests and reflected in the morphology of the hybrids as well. The elaborated antimicrobial hybrid coatings are characterized with good fixation on various samples and wares, good strength, elasticity; they do not change the colour during photo- and isothermal aging and have a number of applications.

**Keywords:** arsenic trioxide, secondary resources, antimicrobial, coating, properties

### INTRODUCTION

Increased concern to the antimicrobial safety in the various spheres is an issue of global importance. In response to the deterioration of ecological conditions, the increasing bacterial and fungal population on various surfaces stimulates a series of biocorrosive processes that cause significant economic losses to industry and pose serious threats to cultural heritage (historic buildings and monuments, archaeological patterns, museum exhibits, etc.) as well [1].

Bacterial corrosion is a result of synergistic interactions between the various materials surfaces, abiotic corrosion products, microbial cells and their metabolites [2]. Pathogenic microorganisms are placed on the surfaces of various natural and synthetic materials (leather, wood, plastics), polymers, and stimulate irreversible deterioration of their physical and mechanical properties, biodegradation and finally, damaging. That affects many fields of technique and industry and causes losses annually amounting to billions of dollars [3, 4].

The development of new type inorganic-organic multifunctional hybrid materials has the real prospect to solve this problem [5]. Antimicrobial covering/protecting of various natural and synthetic materials and wares will also achieve the protection of humans in case of their direct contact with the

surfaces of aforementioned materials and will solve a number of environmental problems.

During the last two decades the design of polyfunctional inorganic-organic antimicrobial hybrid materials has attracted considerable research interest. The wide range of possible hybrids may include innovative combinations, starting from organic and organometallic molecules to inorganic compounds, biogenic transition metals complex compounds or clusters, dispersed in a polymer matrix [6].

Hence, the exploration of new antimicrobial compounds and materials has a great actuality and needs further development for effective prevention and/or inhibition of the growth of detrimental microorganisms and control of biocorrosion processes [6].

Arsenic and its compounds have long been identified for their bactericidal effects and thus they are mainly used in the production of pesticides, anthelmiths, wood preservatives, etc. In addition, arsenic compounds have a long history of use in medicine. Since arsenic trioxide ( $As_2O_3$ ) was first approved by the FDA as the front line therapy for acute promyelocytic leukemia 25 years ago, its anti-cancer properties for various malignancies have been under intense investigation [7, 8].

It is very important to search a cheap base for creating the materials mentioned above on a wide scale, especially from natural and industrial secondary resources. Caucasus region (Georgia) is

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rich in natural resources. Among them arsenic takes a special place [9, 10].

Arsenic deposits are basically situated in the north region of Georgia in the form of occurrences. It is very important that these ores do not contain impurity elements, and the best chance is given to produce highly pure metal arsenic and As<sub>2</sub>O<sub>3</sub>.

Nanotechnology is currently growing as a multidisciplinary field of science and has proved its potential by fetching benefits in modern functional coatings development. The coatings containing nano-particles offer much better material and processing properties than conventional coatings (e.g. increased indentation resistance, high elasticity, fast drying, and no expansion after contact with water, high water vapour permeability).

Thus, a number of environmental benefits are to be expected from nanotechnology-based coatings including: a) thinner coating layers; b) minimization or substitution of solvents and toxic compounds used in coating materials; c) less consumption of energy and cleaning agents; d) extended life span of the coated objects, etc.

#### EXPERIMENTAL

Polyurethane was obtained by interaction of 4,4-dimethylmethanediisocyanate with oligobutylene glycol adipinate in an equimolar ratio. Silicon organic oligomers –  $\alpha,\omega$ -dihydroxydimethyl-(methylvinyl)oligoorganosiloxane ( $\eta=2.7$  Pa·s;  $M_{\text{ebul}} \approx 2.95 \cdot 10^4$ ), bis(hydroxyalkyl)oligodimethylsiloxane ( $M_n \approx 5.600$ ) and oligo[dimethylsiloxane-co-(3-aminopropyl)methyl]siloxane were obtained from Aldrich Chemicals.

*Antimicrobial coating - sample preparation:* to the cyclohexanone solution (155°C) of the PU matrix a definite amount (3, 7, 10 wt.%) of the selected silicon-organic modifiers and bioactive component were gradually added and were stirred for 30-40 min (25°C) until formation of light coloured homogenous mass. Obtained materials were deposited as thin layers on the surface of the various substrates (wood, Teflon) and were left in the air during 48-72 h (25°C) to produce homogenous and smooth protective layers.

*Differential scanning calorimetric measurements* were performed with DSC 200 (Netzsch, Germany). All tests (10 mg of each sample) were conducted under dry nitrogen; temperature range from -100°C to +300°C; heating rate 5°C/min.

*Thermogravimetric analysis* was carried out using Perkin Elmer TGA-7; 10-20 mg of each dry sample was tested [11]. Temperature range 30-700°C; heating rate 10°C/min.

*Hydrophobicity* was studied by a gravimetric method [12].

*Tribological characterization:* Scratch and sliding wear tests were performed on a Micro-Scratch Tester (MST) applying linearly increasing force in the range of 0.03-30.0 N or else a constant force (25°C) [13]. The sliding wear (SWD) results were obtained by multiple scratching with a diamond tip along the same groove. Both in single scratching or in SWD, one obtains the penetration depth  $R_p$  and the residual (healing) depth  $R_h$  determined two minutes later. Both  $R_p$  and  $R_h$  values were taken at the midpoint. The viscoelastic recovery  $\varphi$  was defined by equation (1) which applies to the single scratch resistance tests, as well as to the sliding wear:

$$\varphi = \frac{R_p - R_h}{R_p} \times 100\% \quad (1)$$

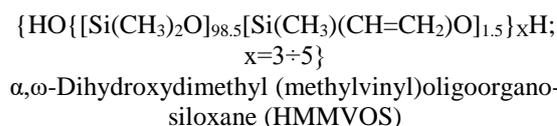
*Dynamic friction* was measured using Nanovea pin-on-disk tribometer. 440 steel balls made by Salem Specialty Balls with 3.2 mm diameter were used. Temperature 20±2°C, speed 100 rpm, sliding distance 40 m, radius 2.0 mm, load 2.0 N, 2000 revolutions, test duration 20 min.

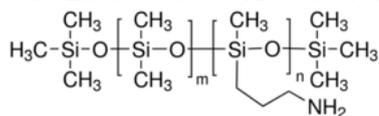
*The scanning electron microscope* (Eclipse ME 600, Nikon) was used to observe the changes in the wear tracks after testing and to study the possible modes of failure or deformation.

#### RESULTS AND DISCUSSION

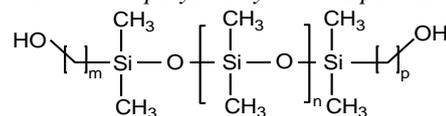
For creation of antimicrobial hybrid coatings nano-sized As<sub>2</sub>O<sub>3</sub> (3 and 5 wt.%) obtained by transformation of arsenic secondary resources were used as the bioactive component (BC) [14-17]. By using non-realized secondary resources it is possible to elaborate relatively cheap bioactive components and inorganic-organic hybrid antimicrobial coatings based on them for protection of the rich cultural heritage in this region.

As polymeric matrix polyurethane (PU) was selected considering its mechanical and tribological properties [18,19]. For modification of some characteristics (elasticity, formation of homogeneous films on various substrates, hydrolytic and thermal stability) of the basic polyurethane matrix polyoligoorganosiloxanes with functional groups (hydroxy-, amino-) at the silicon atom were used:





Oligo[dimethylsiloxane-co-(3-aminopropyl)methyl]siloxane (ODMAPMS)



Bis(hydroxyalkyl)oligodimethylsiloxane (BHODMS)

**Table 1.** Polyurethane composites for antimicrobial coatings

Polymer matrices and hybrid composites	
1. PU	8. PU/10 wt.% ODMAPMS
2. PU/3 wt.% HMMVOS	9. PU/7 wt.% BHODMS
3. PU/3 wt.% As <sub>2</sub> O <sub>3</sub>	10. PU/10 wt.% BHODMS
4. PU/5 wt.% As <sub>2</sub> O <sub>3</sub>	11. PU/7 wt.% ODMAPMS/3 wt.% As <sub>2</sub> O <sub>3</sub>
5. PU/3 wt.% HMMVOS/3wt.% As <sub>2</sub> O <sub>3</sub>	12. PU/10 wt.% ODMAPMS/3 wt.% As <sub>2</sub> O <sub>3</sub>
6. PU/3 wt.% BHODMS	13. PU/7 wt.% BHODMS/3 wt.% As <sub>2</sub> O <sub>3</sub>
7. PU/7 wt.% ODMAPMS	14. PU/10 wt.% BHODMS/3 wt.% As <sub>2</sub> O <sub>3</sub>

Differential scanning calorimetric (DSC) method was used to locate the crystalline phases, glass and phase transition temperature regions of the modified matrices and the hybrid polymer composites obtained on their basis.

DSC studies showed that all tested materials are amorphous (no exothermic peak characteristic for crystallization is displayed on the DSC diagrams) and no melting transitions are visible. Endothermic peaks on the obtained DSC diagrams correspond to glass transition regions ( $T_g$ ). It was shown that tested hybrids have glass transition in the range from +38.8°C to +59.7°C. This is important for the use of the obtained coatings for protection of museum exhibits since optical clarity at room temperature or in a wider temperature range is assured. Doping of nano sized arsenic trioxide as bioactive component into the basic polymer has no significant influence on the value of  $T_g$ . Glass transition temperature regions are more sensitive towards siloxane modifiers. In particular, by incorporation of oligoorganosiloxanes into the researched composites provokes a decrease of  $T_g$  from 58.7-56°C to 38.8-44.3°C.

DSC study also showed phase transition in the glassy state, so called  $\beta$ -transitions ( $T_\beta$ ) [20]. It was established that addition of bioactive component into modified polymer composites reduces the absolute value of  $T_\beta$  from -56°C to -(48-51)°C. Thus, adding 3 wt.% of As<sub>2</sub>O<sub>3</sub> to PU results in lowering of the  $\beta$ -transition temperature  $T_\beta$  centered around the regions from -43.6°C to -37°C correspondingly (Table 1, comp. 1, 2, 5, 13, 14). Thus, addition of BCs enhances the stability of the low-temperature amorphous phase.

Decomposition behaviour and thermal stability parameters of pure and modified hybrid composites were determined by thermogravimetric analysis as follows: initial degradation temperature ( $T_{In.dec.}$ ), decomposition temperature ( $T_{dec.}$ ) with corresponding weight loss (wt.%) and temperature of the maximum rate of degradation ( $T_{max.}$ ), - temperature after which no changes are observed.

Intensive destruction process of the pure PU matrix takes place in the temperature range of 290-460°C with a large weight loss of 81.3% of the original weight. In the 460-570°C range weight drop of the remaining weight is seen (Table 2).

**Table 2.** TGA data of the PU hybrids

Hybrid	$T_{st.dec.}$ , °C	$T_{In.dec.}$ , °C	Weight loss, %	$T_{max.}$ , °C
1	280	290-460	81.3	570
2	285	320-480	36.0	590
4	290	420-532	62.7	685
5	330	410-538	31.4	670
6	300	355-548	27.1	630
7	315	360-390	78.8	580
8	320	360-400	80.0	590
9	320	360-420	77.1	590
10	290	330-480	78.3	580
12	340	360-490	74.3	590
14	340	380-530	75.1	600

PU-composites modified by polyoligoorganosiloxanes are quite stable up to 290-340°C and weight loss does not exceed 5-6 wt.% (Table 2).

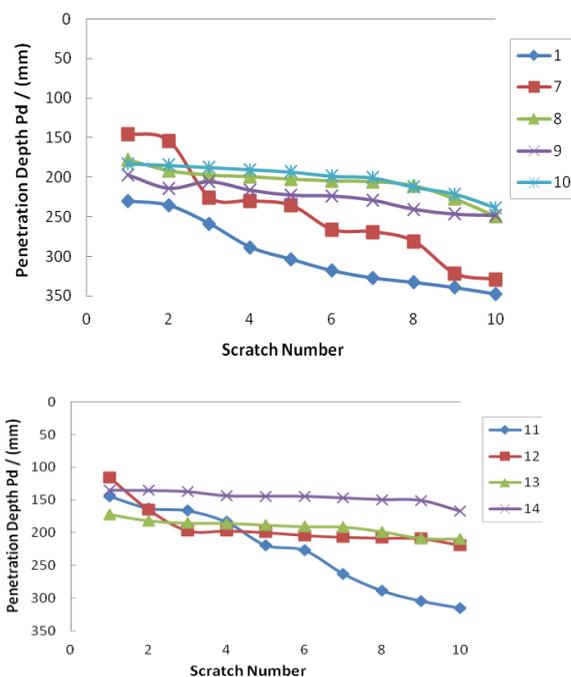
Intensive destruction process of modified samples takes place in the range of about 320-548°C. As is seen in Table 2, both  $T_{st.dec}$  and  $T_{max}$  of the modified polymer hybrids increased with respect to pure PU. Further addition of BC shifts  $T_{In.dec.}$  to the higher temperatures with reduced weight loss. The full thermal degradation of modified hybrid composites is observed in the range of 580-685°C.

Tribological characterization of materials deals with friction, wear, scratch resistance and design of interactive surfaces in relative motion [21]. The basic tribological and surface properties (morphology, outward appearance, optical stability) of the obtained non-modified and modified PU composites and materials were studied.

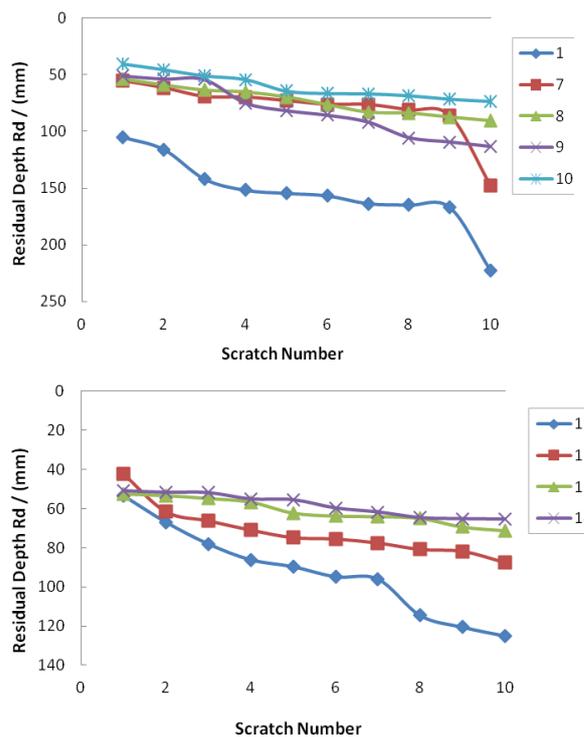
Penetration depth ( $R_p$ ) diagrams of the examined composites at constant load as a function of the number of scratch tests were obtained. Analysis of results showed an improvement of resistance towards instantaneous deformation of the corresponding composites obtained *via* modification of basic polyurethane by siloxane modifiers (Fig. 1; composites 1, 7-10, Table 1). Penetration depths of composites 7-10 are in the range of 200-245  $\mu\text{m}$  while for pure PU  $R_p \approx 298 \mu\text{m}$ . Increasing of wt.% of the used modifier lowers  $R_p$  with respect to the pure PU. Namely, the maximum reductions in  $R_p$  were shown for composites obtained by modification with 10 wt.% of siloxane modifiers -  $R_p$  ranging around 200-206  $\mu\text{m}$  (Fig. 1; comp. 8, 10, Table 1). Herewith the best result showed the modified composite by 10 wt.% BHODMS (Fig. 1; comp. 10, Table 1). Further incorporation of BC slightly lowers  $R_p$  with respect to the pure PU and hybrids (Fig. 1; comp. 11-14, Table 1).

Modifications with silicon-organic oligomers caused a decrease in residual depth ( $R_h$ ) after healing (determined after 2 min) by about 80-90  $\mu\text{m}$  (Fig. 2; comp. 7-10, Table 1). The maximum reduction of  $R_h$  was shown by the composite modified with 10 wt.% BHODMS (Fig. 2; comp. 10, Table 1). For corresponding hybrids a further slight decrease in  $R_h$  was observed as well (Fig. 2; comp. 11-14, Table 1).

The values of viscoelastic recovery ( $\varphi$ ) of modified composites calculated from eqn. (1) are in the range of 60-70%. A slightly higher viscoelastic recovery was registered for PU materials modified with 10 wt.% BHODMS (Fig. 3, comp. 10, 13, Table 1). Thus, improvements in penetration and residual depths, as well of viscoelastic recovery of the examined hybrids with respect to basic PU are manifested.



**Figure 1.** Penetration depths of pure and modified PU composites and antimicrobial coatings (Table 1).

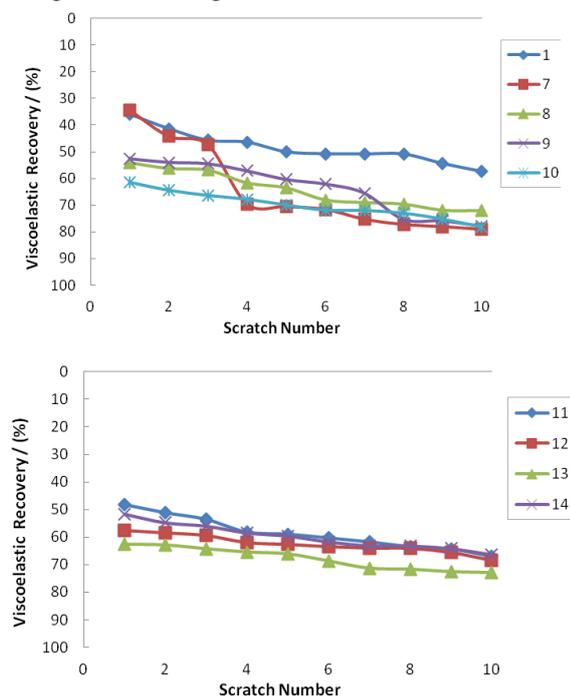


**Figure 2.** Residual depths of pure and modified PU composites and antimicrobial coatings (Table 1).

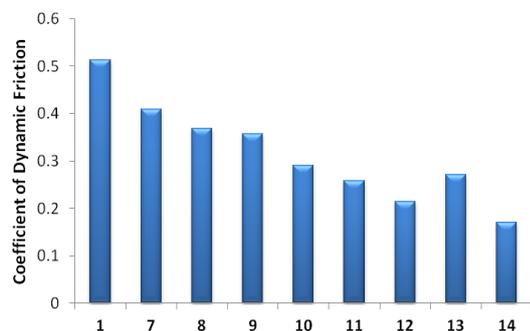
By dynamic friction tests it was shown that modification with ODMAPMS and BHODMS lowers the coefficient of dynamic friction ( $f$ ) of the corresponding composites in respect to pure PU (Fig. 4; comp. 7-10, Table 1). Herewith the increase in modifier's quantity causes an improvement of wear resistance. Accordingly, lower values of the average dynamic friction were

shown by the composite modified with 10 wt.% silicon-organic oligomers with respect to pure PU (Fig. 4; comp. 8, 10, Table 1). Subsequent incorporation of BC shows a further decrease of the values of average friction as a function of composition (Fig. 4; comp. 11-14, Table 1). The hybrid coating obtained by modification with 10 wt.% BHODMS and BC is characterized with the best wear resistance among the tested composites (Fig. 4; comp. 14, Table 1).

The analysis of the dependence of the dynamic friction on the sliding distance mostly shows a steady behaviour of the values of dynamic friction during the tests (Fig. 5).



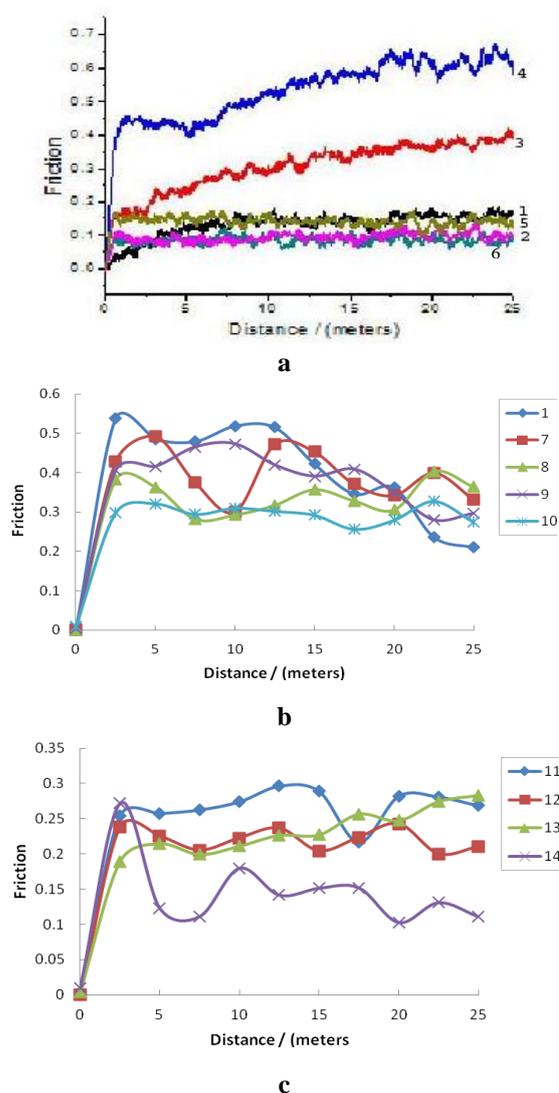
**Figure 3.** Viscoelastic recovery of pure and modified PU composites and antimicrobial coatings (Table 1)



**Figure 4.** Comparison of the values of the average coefficient of dynamic friction for polymer matrices and antimicrobial coatings based on them (Table 1).

The decrease in the coefficient of dynamic friction for PU matrices modified by oligo organosiloxanes is caused by the plasticizer effect of the flexible chains of siloxane modifiers. By

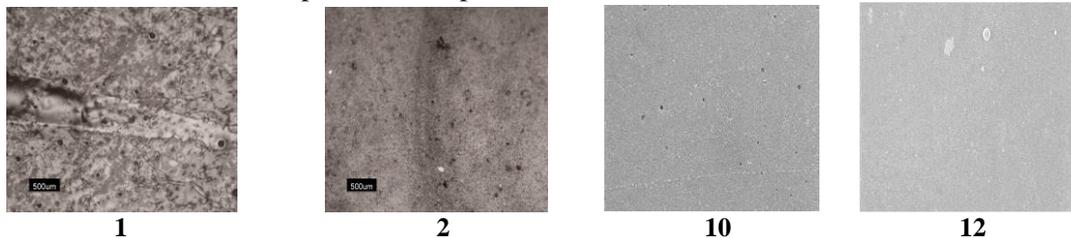
doping of bioactive components into basic PU the coefficient of dynamic friction of the tested coatings slightly increases (Fig. 5; comp. 3, 4, Table 1). Further addition of bioactive component with higher quantities increases the hardness of the formed coatings (Fig. 5; comp. 4, Table 1). Herewith, doping the optimal amount of bioactive component into PU modified with HMMVOS gives satisfying results of wear resistance (Fig. 5; comp. 5, Table 1). Thus, modified polyurethane matrices and corresponding antimicrobial coatings are characterized with lower friction than pure PU. It was established that the wear resistance of the tested composites mainly depends on their composition, on the nature and quantity of modifiers and on the experimental conditions.



**Figure 5.** Dependence of the dynamic friction on the sliding distance for pure and modified PU matrices and corresponding antimicrobial coatings (Table 1).

The obtained results were also confirmed by studying the surface morphology (SEM) of the polymeric matrices and antimicrobial coatings (Fig.

6). Plastic deformation behavior of modified PU films is characterized with less crack nucleation in comparison with non-modified one. Namely, plastic deformation of corresponding films under 2N constant load showed that a split behavior of PU matrix modified by 3 wt.%  $\alpha,\omega$ -dihydroxymethylvinyloligoorganosiloxane is characterized with less crack nucleation in comparison with pure



**Figure 6.** Surface morphology of the PU matrices and antimicrobial coatings (Table 1)

**Table 3.** Hydrophobicity of the PU matrices and corresponding antimicrobial hybrids

N <sub>o</sub>	W <sub>H<sub>2</sub>O</sub> , wt.%	N <sub>o</sub>	W <sub>H<sub>2</sub>O</sub> , wt.%	N <sub>o</sub>	W <sub>H<sub>2</sub>O</sub> , wt.%
1	0.046	6	0.027	11	0.027
2	0.025	7	0.028	12	0.026
3	0.016	8	0.027	13	0.024
4	0.012	9	0.026	14	0.025
5	0.010	10	0.024		

This effect is caused by the plasticizing behaviour of siloxane modifiers.

Hydrophobic properties of coatings play a significant role in the process of adhesion of microorganisms on various surfaces. Water absorption ability (W<sub>H<sub>2</sub>O</sub>, wt.%) of the obtained antimicrobial coatings was determined by a gravimetric method [11]. As performed tests showed, silicon-organic and bioactive inorganic modifiers act as a barrier in the polyurethane matrix, hindering the effective path for the water molecules to travel, and accordingly lead to an increase in water absorption resistance. Thus, W<sub>H<sub>2</sub>O</sub> did not exceed 0.03 wt.% during 720 h in all cases (Table 3). It was established that during three months, under conditions of isothermal aging (40-60°C) and “light-weather” (complex action of air oxygen, carbon dioxide, visible light, moisture) the initial appearance, color, optical transparency and mechanical properties (surface homogeneity without splits formation) of the created anti-biocorrosive coatings were not deteriorated.

Based on the research carried out it was shown that the mechanical, tribological and operational properties of antimicrobial composite and materials were improved by the proper combination of the structure, bioactivity and ratio of basic components. The elaborated antimicrobial coatings are characterized with good fixation on various samples and wares, sufficient strength, elasticity and good tribological properties; they do not

PU. It should be noted that composites obtained by modification of PU with 10 wt.% bis(hydroxyalkyl)polydimethylsiloxane and BC, have smoother surfaces, without brittleness and porous regions and demonstrated the least crack nucleation among the tested polymeric matrices (Fig. 6; comp. 1, 2, 10, 12, Table 1).

scratch easily; do not change the relief of the surface and the colour during photo- and isothermal aging (40-60°C); are relatively cheap, available and safe for human. Bioactive components conferred to the antimicrobial coatings completely new properties. Accordingly, not only covering and antimicrobial protection of various natural and synthetic materials, wares and museum exhibits can be achieved, but meanwhile, the coatings provide removal and annihilation of harmful effects of microorganisms, fungi and bacteria, which also presupposes solving of a number of environmental problems.

## CONCLUSIONS

New generation multifunctional polymer coatings with specific properties were developed by using siloxane oligomers as modifiers of a selected polyurethane matrix. As bioactive component nano-sized arsenic trioxide was used, which is non-volatile, non-flammable, biocompatible with the used polymer matrix and dimensionally stable, obtained by transformation of cheap secondary resources of arsenic production. It was established that the addition of silicon-organic oligomers into the polyurethane matrix modifies the thermal, tribological and operational properties of the corresponding materials in the desired direction. The coatings are characterized with good fixation on various surfaces, strength and elasticity, thermal stability, hydrophobicity and their features and

colour are not worsened during photo- and isothermal aging.

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