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MECHANICAL PROPERTIES OF POLYMER COATINGS CONTAINING HAP AND ACTIVE SUBSTANCE ON A METAL SUBSTRATE

WŁASNOŚCI MECHANICZNE POWŁOK POLIMEROWYCH ZAWIERAJĄCYCH HAP I SUBSTANCJĘ AKTYWNĄ NA PODŁOŻU METALOWYM

Key words: biodegradable polymer coatings, titanium alloys, Pin-On-Disc, scratch test.

Abstract: Titanium alloys are currently widely used in implantation, especially in orthopaedics. However, undesirable reactions caused by aluminium and vanadium ions released from the surface of the most commonly used alloys, Ti6Al4V and Ti6Al7Nb, result in the need to modify the surface of the material to improve biocompatibility. Among the available modification methods, one can mention the application of biodegradable polymer coatings, which, apart from improving biocompatibility by limiting the penetration of alloying element ions into the tissue environment, can also be a matrix for the release of mineral (HAp) and active substances. The paper attempts to determine the mechanical properties of PLGA polymer coatings containing nanoparticle hydroxyapatite and an active substance (dexamethasone) applied with the ultrasonic spray coating method on a Ti6Al7Nb alloy substrate. The scope of the research included: surface topography testing using an optical profilometer, coating adhesion testing to the substrate using the scratch test method and tribological testing (Pin-On-Disc method).

Słowa kluczowe: biodegradowalne powłoki polimerowe, stopy tytanu, Pin-On-Disc, scratch test.

Streszczenie: Stopy tytanu znajdują obecnie szerokie zastosowania implantacyjne, szczególnie w ortopedii. Jednakże niepożądane reakcje wywoływane przez jony glinu i wanadu uwalnianie z powierzchni najczęściej wykorzystywanych w praktyce stopów Ti6Al4V oraz Ti6Al7Nb skutkują koniecznością modyfikacji powierzchni materiału w celu poprawy biokompatybilności. Wśród dostępnych metod modyfikacji wymienić można nakładanie biodegradowalnych powłok polimerowych, które poza poprawą biokompatybilności poprzez ograniczenie przenikania jonów pierwiastków stopowych do środowiska tkankowego stanowić mogą także matrycę dla uwalniania substancji mineralnych (HAp) oraz aktywnych. W pracy podjęto próbę określenia własności mechanicznych powłok polimerowych z PLGA, zawierających nanocząsteczkowy hydroksyapatyt oraz substancję aktywną (deksametazon), nakładanych metodą natryskiwania ultradźwiękowego na podłoże ze stopu Ti6Al7Nb. Zakres przeprowadzonych badań obejmował badania topografii powierzchni z wykorzystaniem profilometru optycznego, badania adhezji powłok do podłoża metodą scratch test oraz badania tribologiczne (metoda Pin-On-Disc).

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INTRODUCTION

According to the Global Burden of Disease Study, in 2019, there were 178 million new fractures (33,4% increase since 1990) and 455 million prevalent cases of acute or long-term worldwide fracture symptoms **[L. 1]**. As the number of fractures increases, so does the number of osteosynthesis performed. This requires searching for the best solutions for implants. However, due to the limited number of metal biomaterials, nowadays, the basic direction of research is the modification of their surface **[L. 2]**.

Due to high corrosion resistance, low density and good biocompatibility in a tissue and body fluids environment, one of the most commonly used biomaterials are titanium alloys. Although, after many years of studies, it was proved that they might cause allergies and other adverse reactions, so they are not fully biologically inert **[L. 3]**. Corrosion resistance can be improved by creating passive layers on the surface of biomaterials, for example, through the anodic oxidation process. However, this does not limit the presence of metal ions, such as titanium or aluminium, which may be released into tissues and body fluids during the degradation process **[L. 4]**.

By limiting the penetration of degradation products into tissue environment, biocompatibility can be improved by applying polymer coatings **[L. 6]**. In addition, a biodegradable polymer can also be a matrix for the delivery of the active substance (biodegradable drug delivery systems) and mineral components as well **[L. 7, 8]**. The local delivery in the fracture zone could reduce systematic drug treatment.

Hydroxyapatite (HAp) is widely used in bone tissue engineering because it resembles the natural inorganic bone component and has osteoconductive properties. Other studies have already reported the promising potential for the clinical application of ceramic hydroxyapatite coatings on titanium alloys **[L. 15]**. Moreover, using electrochemical deposition to apply HAp layers on a metal substrate allows obtaining a coating with the desired properties by modifying the process parameters **[L. 15, 16]**. However, it is brittle and possesses a low resorption rate in vivo. To solve these problems, HAp has been combined with, among others, biodegradable PLGA polymer **[L. 9]**. One of the active substances is dexamethasone (DEX), which, besides being used to treat inflammation, has a wide variety of uses in the medical field. Dexamethasone works by suppressing the migration of neutrophils and decreasing lymphocyte colony proliferation **[L. 5]**.

A promising idea seems to be the application of sandwich-structure coatings consisting of a biodegradable polymer enriched with hydroxyapatite as an inner coating and a polymer with an active substance as an outer coating. In this scenario, in the first phase after implantation, an anti-inflammatory drug is released during the short-term degradation of the external coating. Then, during the long-term degradation of the internal coating, HAp is released to improve the bone healing process. Moreover, polymer coatings on the metal substrate do not limit the bone stabilisation time due to the polymer degradation process. However, due to frictional force occurring in the implant-bone system, the mechanical properties of the coating are significant.

The dip-coating method is one of the most commonly used methods of applying polymer coatings. The ultrasonic spraying method has recently become popular, which involves spraying fine droplets onto the material's surface. This process allows obtaining continuous, homogeneous coatings, characterised by good adhesion to the substrate **[L. 10]**.

Authors **[L. 11, 12]** have already presented results of the properties of PLGA polymer coatings containing HAp on Ti6Al7Nb substrate. Therefore, this study investigated the influence of short-term exposition to the simulated body conditions on the mechanical properties of biodegradable polymer coatings. Moreover, the research aimed to determine the impact of various layers of an external polymer coating containing dexamethasone as an active substance on coatings properties. The scope of the research included topography studies, adhesion of the coatings and tribological tests.

MATERIALS AND METHODS

A Ti6Al7Nb alloy with chemical composition, structure, and mechanical properties complying with ISO 5832-11 recommendations was used as a substrate. The samples were taken from a rod with a diameter of 25 mm. The surface of the substrate was modified by grinding, sandblasting, and anodic oxidation. For the grinding, abrasive papers were subsequently of 120, 300, and 500 grades. Sandblasting was carried out as abrasive for t = 2 min with glass balls of diameter from 70 to 110 µm. Anodisation was performed using a bath based on phosphorous and sulphuric acid (Titan Colour, Poligrat GmbH) at 97 V; t = 2 min. Before the coating process, the samples were purified in 99% isopropanol.

Polymer coatings based on poly(D, L-lactide-glycolide) PLGA(85/15) with hydroxyapatite (HAp) (< 200 nm, Merck) and dexamethasone (DEX) (MCE) have been chosen for the coating materials. PLGA was synthesised in bulk by the ring opening polymerisation of glycolide (Purac) and D,L-lactide (Purac) at 130°C for 24 hours and next, at 120°C for 48 hours at argon atmosphere using Zirconium (IV) acetylacetonate ($Zr(acac)_4$) (Merck) as a non-toxic initiator. The molecular weight of the polymer was 74 kDa.

The ultrasonic spray coating method coated the metallic substrate with the polymer. The solution of 1% PLGA in dichloromethane was enriched with 20% HAp for internal coating. A 1% PLGA solution containing 20% DEX was used as an external coating. The coatings were applied by ExactaCoat (Sono-Tek) with AccuMist™ Ultrasonic Spray Shaping with the following parameters of the process: ultrasound frequency 60 kHz, ultrasound power 1.5 W, solution's flow rate 1 cm^3/min, speed of nozzle motion 10 mm/s, the distance between nozzle and substrate surface 70 mm and air curtain pressure 2 Pa. The inner layer containing hydroxyapatite comprised 15 layers, and the outer layer containing the active substance consisted of 3, 5 or 7 layers. The coated samples were airdried for 3 days at 25°C. Polymer coatings were subjected to 3, 6 and 9 days of exposure to PBS solution (ChemSolve) at 37°C.

The topography of the polymer coatings in the initial state and after exposition to PBS was analysed with 3D Surface Metrology Microscope Leica DCM8 (Leica Microsystem) using the confocal differentiation method.

The tests on the adhesion of the biodegradable polymer coatings to the substrate in the initial state and after 3, 6 and 9 days of exposition were performed by the scratch test method, using an open platform with the MicroCombi Tester by CSM (Anton Paar). A diamond Rockwell cone intender was used for the study. The loading force increased from 0.03 to 30 N. The force load rate was 10 N/min, the table travel speed was 1 mm/min, and the scratch length was 3 mm. Due to the difficulty in estimating the critical force F_n, a comparison of the obtained friction force as a function of the scratch length for the non-coated and coated samples was proposed using microscopic observation. The first intersection point of the curves was treated as the force causing delamination of the coating. Three measurements were taken on each sample.

The pin-on-disc method performed tribological tests using a TRB^3 tribometer (Anton Paar). A stainless steel ball with a diameter of 6 mm was used as a counter-specimen, and a normal load was 6 N. The measurements were carried out until the breaks of the coating. A non-coated Ti6Al7Nb sample was used as a reference. The specific wear rate was determined using Formula (1), where V_w is the wear volume (mm^3), F is the normal load (N), S is the total sliding distance (m):

$$W = \frac{V_w}{F \times S} \quad (1)$$

The wear volume was calculated from the cross-sectional area of the abrasive using 3D Surface Metrology Microscope Leica DCM8.

RESULTS AND DISCUSSION

Typical images of the coating surfaces are shown in **Fig. 1**, and the values of the Sa parameter are shown in **Fig. 2**. In the initial state, biodegradable polymer coating consisting of 3 PLGA with DEX layers was characterised by the lowest value of the Sa parameter, and the highest roughness was observed in the 5-layer coating. This indicates an ambiguous effect of the number of coatings on the surface roughness. Exposure to the PBS solution causes an increase in roughness in all cases. For 3-layer biodegradable polymer coatings with dexamethasone, the highest increase in roughness was noted after 6 days of exposure, while after 9 days, the Sa value remained similar. The coating consisting of 5 and 7 layers showed the highest increase in the Sa parameter after 9 days. In the case of a 7-layer coating, the increase in roughness was most significant. The observed changes in roughness may indicate the progressive degradation of the polymer, which is the goal of the use of biodegradable polymer coating and has also been reported in other studies **[L. 13]**.

The force causing delamination of the coating was obtained by comparing diagrams of the friction force as a function of the scratch length of the applied polymer coatings and Ti6Al7Nb substrate. The critical force was determined as the value of the measured force at the intersection of the courses (**Fig. 3**).

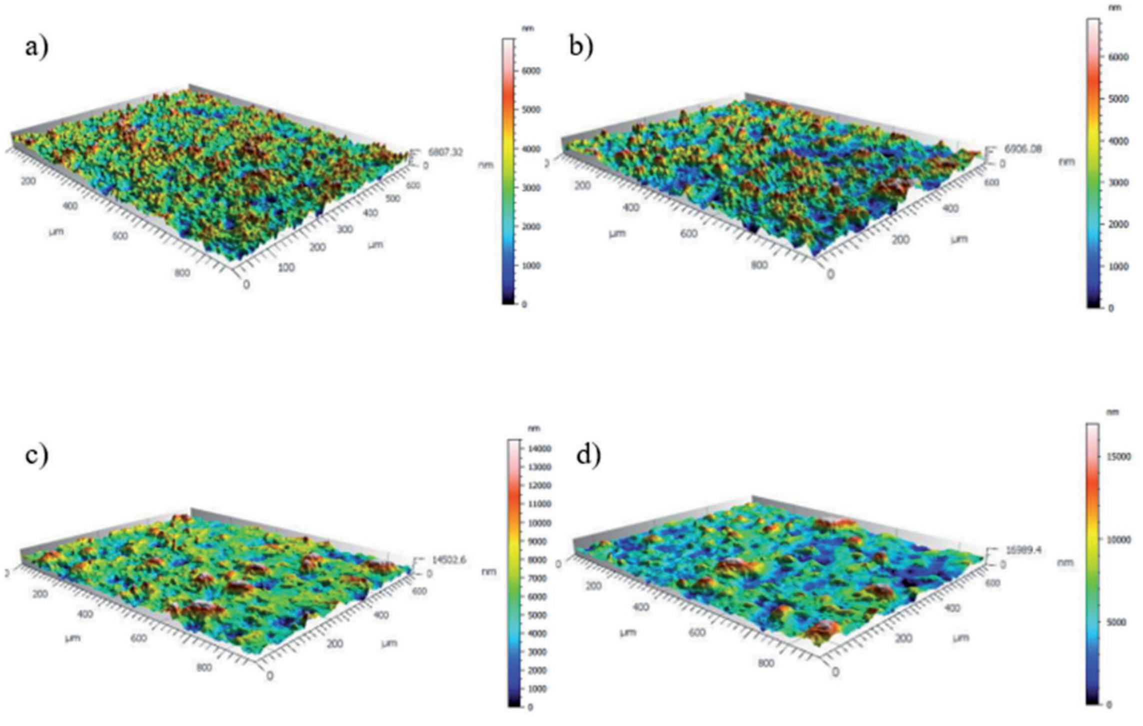

Fig. 1. A typical 3D image of the surface of the PLGA with DEX coating composed of 3 layers: a) in the initial state, b) after 3 days of exposure, c) after 6 days of exposure, and d) after 9 days of exposure

Rys. 1. Przykładowe obrazy 3D powierzchni powłoki PLGA zawierającej DEX złożonej z 3 warstw: a) w stanie wyjściowym, b) po 3 dniach ekspozycji, c) po 6 dniach ekspozycji, d) po 9 dniach ekspozycji

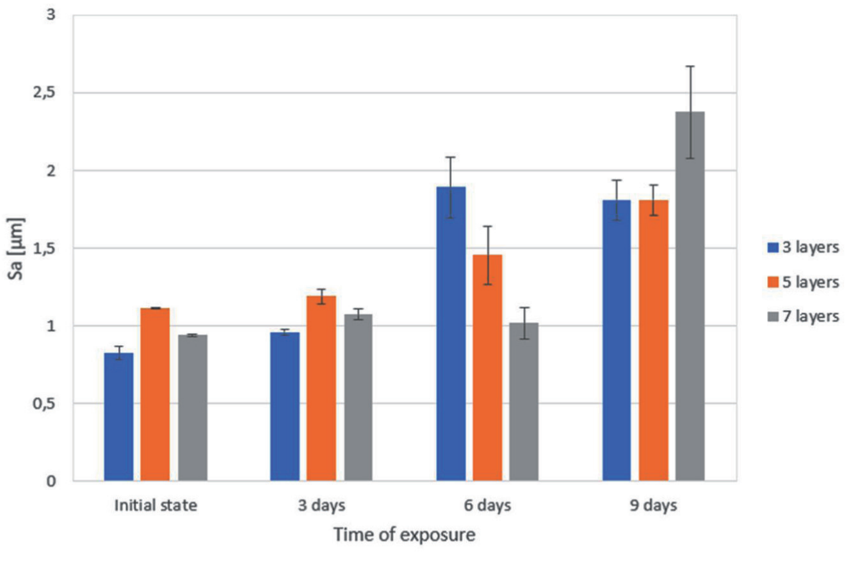

Fig. 2. The mean values of the Sa parameter of the coatings in the initial state and after exposure to the PBS solution

Rys. 2. Średnie wartości parametru Sa powłok w stanie wyjściowym oraz po ekspozycji na działanie roztworu PBS

Comparing the results of adhesion tests (**Tab. 1**) shows that a similar value of the critical force characterised all the analysed coatings in the initial state. However, it was observed that with the increase in the number of layers, the adhesion of the coating decreased, which may be related to the polymer sticking to the indenter during the test.

Three days of exposure to the PBS solution resulted in a slight decrease in the force, causing delamination in all analysed samples. After 6 days

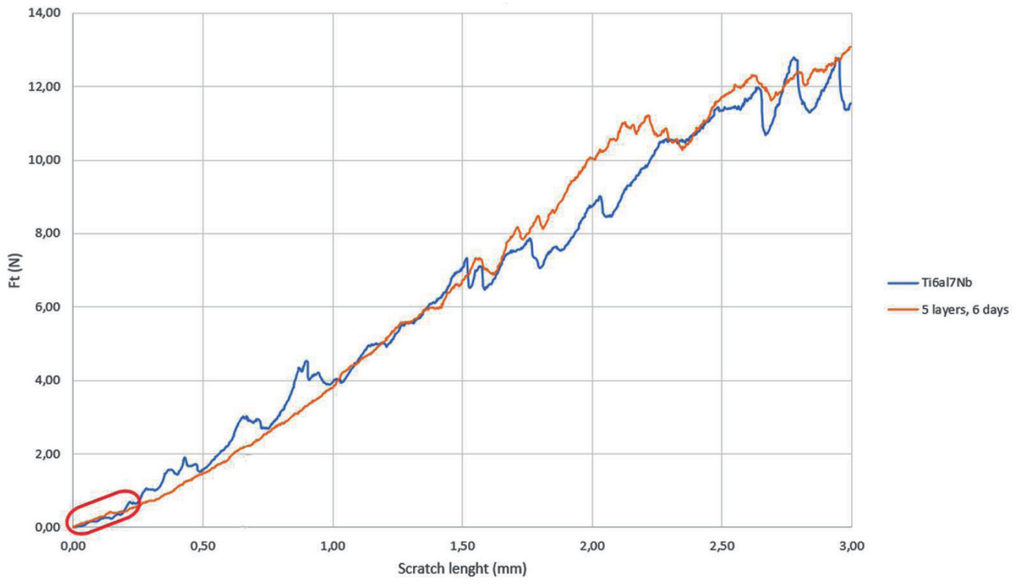

Fig. 3. An exemplary graph of the friction force as a function of the scratch length
Rys. 3. Przykładowy wykres siły tarcia w funkcji długości zarysowania

of exposure, a further decrease in the critical force was observed for polymer coatings consisting of 5 and 7 layers. On the other hand, the 3-layer coating showed a slight increase. In addition, an increase in the critical force value was observed after 9 days of exposure to the PBS for 3- and 5-layers coatings. After this time, the force value decreased only for a 7-layer biodegradable polymer coating. However, the obtained results do not indicate a significant effect of exposure to the PBS solution on the adhesion of polymer coatings to the substrate, which can be caused by short-term exposure. In other research **[L. 14]**, an increase in the critical force during the first stage of exposure was observed, and prolonged degradation decreased the adhesion of biodegradable polymer coatings to a metal substrate.

The coefficient of friction diagrams from the tribological test is shown in **Fig. 4, 5** and **6**. Regardless of the number of polymer coating layers, it was observed that the application of PLGA polymer coating decreases the value of the coefficient of friction in reference to the Ti6Al7Nb substrate. In the initial state, the values of the friction coefficient for the 3- and 7-layer coatings were similar, and a lower coefficient characterised the 5-layer coating. However, in the case of the 7-layer coating, the sliding distance was shorter than in the other specimens. After 3 days of exposure, the coefficient of friction increased in all cases, while after 6 days, it decreased. There was no decrease in the coefficient of friction after 9 days of exposure, but the sliding distance of all variants was significantly shortened.

Table 1. Test results of the adhesion of biodegradable polymer coating to the substrate
Tabela 1. Wyniki badania adhezji biodegradowalnych powłok polimerowych do podłoża

Fn [N]			
Time of exposure \ Number of layers	3 layers	5 layers	7 layers
Initial state	2.66(24)	2.36(13)	2.24(18)
3 days	2.02(10)	2.14(21)	2.13(16)
6 days	2.09(34)	2.06(12)	1.97(11)
9 days	2.30(23)	2.45(44)	1.84(15)

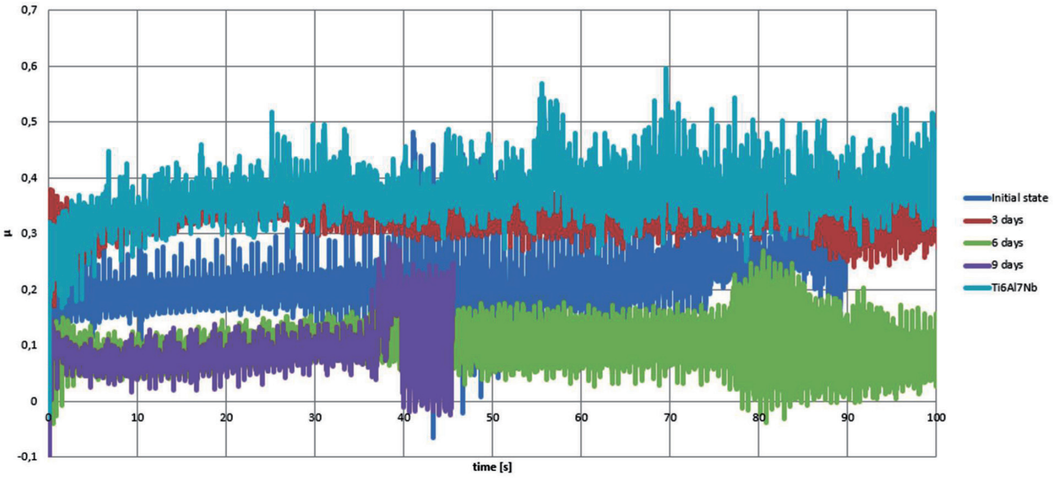

Fig. 4. Graph of the coefficient of friction (µ) of a PLGA polymer coating containing DEX, consisting of 3 layers
Rys. 4. Wykres współczynnika tarcia powłoki polimerowej PLGA zawierającej DEX, składającej się z 3 warstw

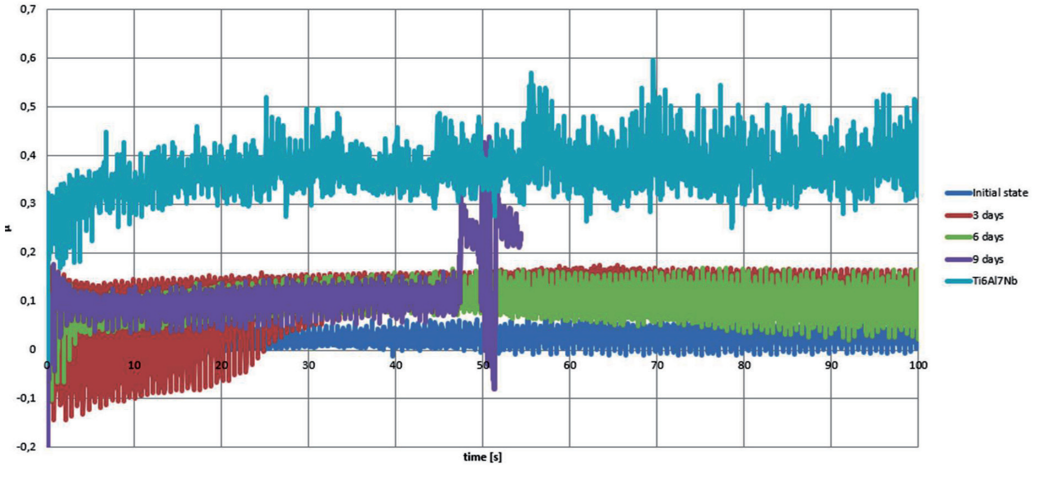

Fig. 5. Graph of the coefficient of friction (µ) of a PLGA polymer coating containing DEX, consisting of 5 layers
Rys. 5. Wykres współczynnika tarcia powłoki polimerowej PLGA zawierającej DEX, składającej się z 5 warstw

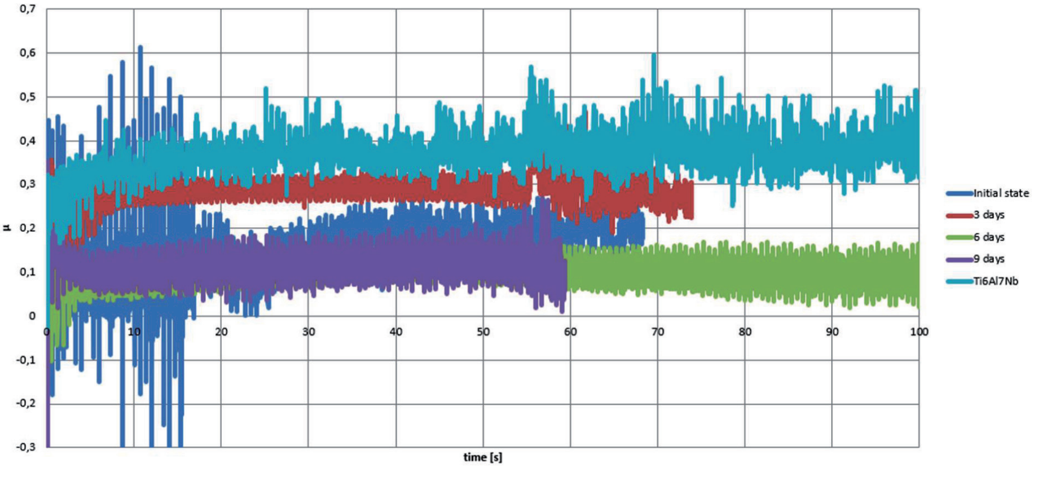

Fig. 6. Graph of the coefficient of friction (µ) of a PLGA polymer coating containing DEX, consisting of 7 layers
Rys. 6. Wykres współczynnika tarcia powłoki polimerowej PLGA zawierającej DEX, składającej się z 7 warstw

The wear resistance parameters are shown in **Table 2**. The lowest values of wear volume and specific wear rate are characterised by samples in the initial state, regardless of the variant of the number of coatings. In the case of a 3-layer coating, the wear resistance decreases with increasing exposure time, except after 9 days when it is slightly higher compared to 6 days. Wear volume increases with time. The wear resistance of a 5-layer coating decreases after 3 days of exposure and then increases until the exposition to PBS solution ends. Wear resistance decreased, and the wear volume increased over time for a 7-layer coating.

Based on the analysis **(Fig. 7)** of the wear tracks of the coatings, in the initial state, the wear track width of all samples was similar and was approximately 600 µm. The abrasion width of the 3- and 7- layer coating increases over time to a value of about 1000 µm after 9 days of exposure. The wear track of the 5-layer polymer coating reaches its greatest width after 3 days and then decreases to around 600 µm again. In all analysed specimens, the protruding areas on the surface were attributed to the accumulation of wear debris.

Table 2. Results of the tribological tests
Tabela 2. Wyniki badań tribologicznych

Number of layers	Time of exposure	Wear volume Vw (mm^3)	Specific wear rate W (mm^3/Nm)
3 layers	Initial state	0.02	0.02
	3 days	0.32	0.28
	6 days	0.53	0.75
	9 days	0.95	0.39
5 layers	Initial state	0.18	1.01
	3 days	1.26	5.99
	6 days	0.68	2.12
	9 days	0.41	0.05
7 layers	Initial state	0.03	0.04
	3 days	0.04	0.2
	6 days	0.65	0.88
	9 days	1.13	0.96

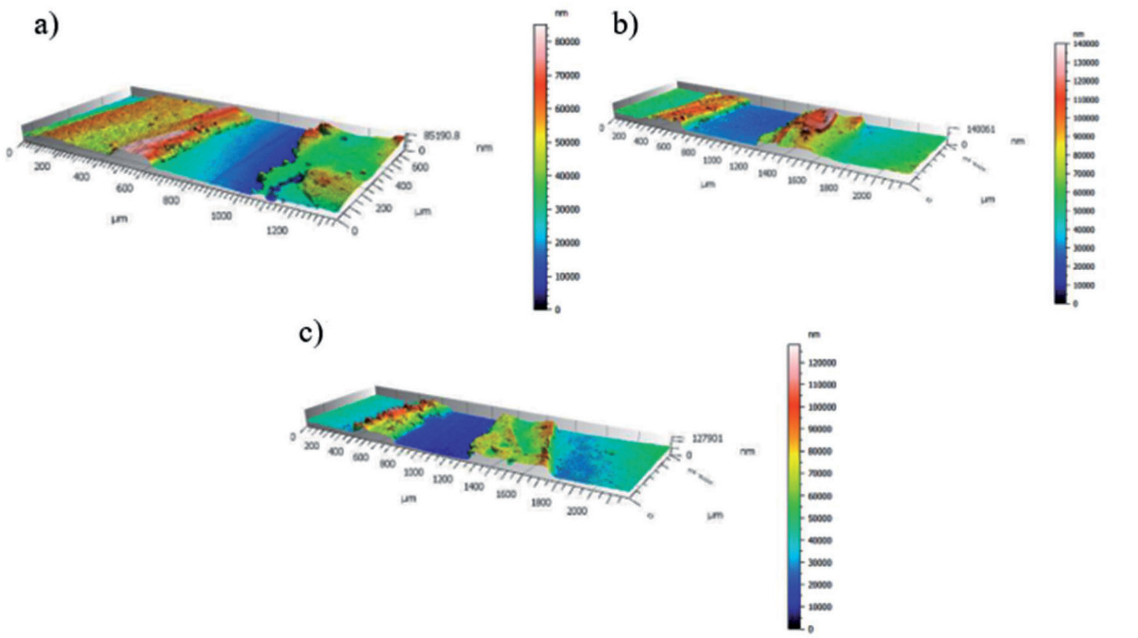

Fig. 7. Surface topography of PLGA polymer coatings containing DEX after tribological tests: a) consisting of 3 layers, b) consisting of 5 layers, c) consisting of 7 layers, after 3 days of exposure to PBS solution
Rys. 7. Topografia powierzchni powłok polimerowych PLGA zawierających DEX po badaniach tribologicznych: a) składającej się z 3 warstw, b) składającej się z 5 warstw, c) składającej się z 7 warstw, po 3 dniach eskpozycji na działania roztworu PBS

CONCLUSIONS

A different number of layers of biodegradable polymer coating enriched with dexamethasone were applied as an external coating on the Ti6Al7Nb substrate, previously coated with a PLGA containing hydroxyapatite. The work aimed to determine the most advantageous variant of the coating. This research showed that the exposition to simulated body fluid increased the roughness of the polymer coatings. Moreover, short-term exposure does not significantly affect the adhesion of biodegradable PLGA polymer coatings to the Ti6Al7Nb substrate. However, the duration of exposure decreased wear resistance with the exception of a 5-layer coating, where the effect of exposure time is ambiguous.

By comparing the obtained results, it can be concluded that the best variant of the biodegradable PLGA polymer coating with DEX consists of 5 layers. However, the results obtained in this work are only one of the criteria. This issue requires further research, in particular studies of polymer degradation and dexamethasone release kinetics, to select a variant with the most desirable coating properties, affecting the best possible therapeutic effect.

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