

Biodegradable polymer coatings on Ti6Al7Nb alloy

JANUSZ SZEWCZENKO^{1*}, WOJCIECH KAJZER¹, ANITA KAJZER¹, MARCIN BASIAGA¹,
MARCIN KACZMAREK¹, MAGDALENA ANTONOWICZ¹, KATARZYNA NOWIŃSKA²,
JOANNA JAWORSKA³, KATARZYNA JELONEK³, JANUSZ KASPERCZYK³

¹ Silesian University of Technology, Faculty of Biomedical Engineering,

Department of Biomaterials and Medical Devices Engineering, Zabrze, Poland.

² Faculty of Mining and Geology, Department of Applied Geology, Gliwice, Poland.

³ Centre of Polymer and Carbon Materials of the Polish Academy of Sciences Zabrze, Poland.

The aim of the study was to determine the influence of long term exposure to Ringer's solution of biodegradable polymer coatings containing an active substance on the Ti6Al7Nb alloy substrate on the physical and chemical properties of the coatings and the degradation process of the metal substrate. The studies used poly(L-lactide-co-trimethylene carbonate) P(L/TMC), poly(L-lactide-co-trimethylene carbonate-glycolide) P(L/TMC/G) and poly(D,L-lactide-glycolide) (PLGA) coatings applied to the anodically oxidized Ti6Al7Nb alloy by means of dipping method (1, 2 and 3 dips). The polymer coatings contained ciprofloxacin. Roughness and wettability tests were carried out on the substrate and polymer coatings, the pitting corrosion resistance of the substrate and samples with polymer coating was determined, the number of metallic ions released to the solution from the coated and uncoated samples was determined as well as the adhesion of polymer coatings. The research was supplemented by microscopic observations. The results of the research indicate different influence of exposure to Ringer's solution on the physical and chemical properties of biodegradable polymer coatings containing ciprofloxacin and the course of the degradation process of the metal substrate.

Key words: Ti6Al7Nb, biodegradable polymer coating, wettability, corrosion resistance, ion release, adhesion of polymer coatings

1. Introduction

Due to the limited number of metal biomaterials commonly used for implants and their limitations, currently the basic direction of research is the modification of their surface [1], [25]. Its main goals are the improvement of biotolerance and functionalization aimed at improving the quality of the adhesion between the implant and the surrounding tissues [16], [24]. One of the most commonly used metal biomaterials are titanium alloys, whose surface is modified by the production of passive coatings. The most commonly used method is anodic oxidation, which results in a homogeneous continuous passive layer. It provides high corrosion resistance in the environment of tissues and body fluids, however, it does not eliminate the degra-

dation process, which, in the case of Ti6Al4V and Ti6Al7Nb alloys, results in the presence of vanadium and aluminium ions [2], [12], [13], [21], [22].

One of the methods of surface modification of metal biomaterials may be the use of polymer coatings. They improve the biotolerance of implants, and when using biodegradable polymers they can be a matrix for the release of active substances [9], [10], [20]. The use of suitable polymers with known degradation kinetics can be used for the controlled release of active substances [17], [18], [23]. The result could be the reduction of systemically used drugs, caused by local delivery in the treatment zone together with a metal implant stabilizing the surrounding tissues. The limitation of the use of implants made exclusively of biodegradable polymers is the process of their degradation, resulting in the loss of their mechanical properties. However, their

* Corresponding author: Janusz Szewczenko, Silesian University of Technology, Faculty of Biomedical Engineering, Department of Biomaterials and Medical Devices Engineering, ul. Roosevelta 40, 44-800 Zabrze, Poland. E-mail: janusz.szewczenko@polsl.pl

Received: August 27th, 2019

Accepted for publication: October 10th, 2019

use on the surface of the metal substrate does not limit the time of stabilization.

Degradable aliphatic poly(trimethylene carbonate) (PTMC) as well as poly(carbonate-co-esters) of trimethylene carbonate (TMC) with lactide and glycolide are interesting materials and present great interest for applications in the fields of surgery, tissue engineering and sustained drug delivery [4], [5], [7]. The huge interest of biodegradable materials requires the tailoring of physicochemical properties of the polymers for particular application. Copolymerization is widely used for modification of the polymer properties in order to obtain desired material characteristics in the final products [26]. It is possible to obtain drug delivery systems with different properties by choosing copolymers obtained from various comonomeric units. Poly(L-lactide) (PLLA) is a crystalline polymer which degrades very slowly by hydrolytic degradation and random scission of ester bonds via the bulk erosion mechanism. The rate of PLLA degradation is very low because of its high hydrophobicity and is also much slower than polyglycolide. Poly(D,L-lactide) (P(D,L-LA)) is an amorphous polymer and, compared to PLLA, it shows faster degradation rate. Copolymers of lactide and glycolide are synthesized in order to obtain materials with modified properties. They are commercially available with a variety of physico-chemical characteristics [26]. P(TMC) undergoes surface erosion *in vivo* and is characterized by a very slow *in vitro* degradation, without the release of acidic products [3]. Materials based on P(TMC) has excellent flexibility but poor mechanical strength. Copolymerization with lactide may change the properties of P(TMC) – it may improve its mechanical properties. Materials based on PTMC which were prepared from TMC and D,L-lactide or ϵ -caprolactone were shown to be compatible with a large number of cells [8]. There are numbers of commercial products available on the market today based on aliphatic polyester or polyestercarbonate such as: sutures, fixation devices, screws, pins, drug delivery systems [6], [19]. In spite of the fact that PLGA is the most frequently used biodegradable polyester, other materials with different comonomer, such as: lactide, glycolide or trimethylene carbonate have proven its usefulness, e.g., as drug-eluting coatings [20].

The aim of the work was to determine the influence of modification of the oxidized Ti6Al7Nb alloy with biodegradable polymer coatings P(L/TMC), P(L/TMC/G) and PLGA enriched with ciprofloxacin on physical and chemical properties of the coatings and the substrate. The influence of coating parameters (number of dips) and exposure to Ringer

solution was analyzed. In particular, the topography and wettability of the surface, the corrosion resistance of the metal substrate, the number of ions released to the corrosive environment and the adhesion of the coatings to the metal substrate were determined. Conducted studies were supplemented by microscopic observations.

2. Materials and methods

The material used in the tests was Ti6Al7Nb alloy with chemical composition, structure and mechanical properties complying with ISO 5832-11 recommendations. The samples in the form of discs were taken from rods of 24 mm in diameter and rods with a diameter of 6mm and a length of 60 mm. The surface of the samples was modified by applying grinding, sandblasting and anodic oxidation. For grinding, the abrasive papers, subsequently of 120, 300 and 600 grade were used. For sandblasting, glass balls of diameter from 70 to 110 were used; $t = 2$ minutes. Anodization was carried out with the use of the electrolyte based on phosphorous and sulfuric acid at the voltage 97 V; $t = 2$ minutes.

Different kinds of polymers have been used to prepare the matrix with ciprofloxacin: poly(L,L-lactide-trimethylene carbonate) (74/26) P(L/TMC), poly(lactide-trimethylene carbonate-glycolide) (10/12/78) P(L/TMC/G), poly(D,L-lactide-glycolide)(84/16) PLGA copolymers were synthesized in bulk by the ring opening polymerization (ROP) of ϵ -caprolactone, glycolide, trimethylene carbonate, L-lactide and D,L-lactide: at 150 °C for 27 h (P(L/TMC)) and at 120 °C for 72 h (PLGA, P(L/TMC/G)) at argon atmosphere using Zirconium(IV) acetylacetonate ($Zr(acac)_4$), as a non-toxic initiator with an initiator/monomers molar ratio of 1/1200. The obtained materials for purification were dissolved in chloroform and precipitated in cold methanol. Finally, the purified materials were dried in a vacuum at room temperature to constant weight.

Polymer solutions (1% w/w, solvent: CH_2Cl_2) have been used to coat the metallic samples by dipping method (Dip Coater, MTI Corporation, 1, 2, 3 layers, 30 s of immersion time, 15 min of delay between dips). Coated samples were dried for first 3 days in the air, and then for one week, under reduced pressure.

The morphology of the samples before and after the exposure to the Ringer's solution was analysed using stereoscopic microscope Zeiss Stereo Discovery V8 with digital camera MC5s. Study of the metal

substrate surface was carried out using the Sensofar Sneox profilometer. Combination of two scanning techniques was applied: confocal and focal differentiation for each measured frame (Confocal Fusion). Light with a length of 530 nm and a 20× magnification lens were used. The study was carried out on the surface of $1620.24 \times 1217.76 \mu\text{m}$. The tests were carried out for both the non-coated samples (substrate) and the samples with polymer coatings in the initial state and a 3-month exposure to the Ringer's solution.

To determine the wettability of a surface, contact angle was performed on the selected samples. Contact angle measurements (θ_w) were conducted using drop of distilled water of the volume of 1.5 ml. The measurements were performed by applying the SURFTENS UNIVERSAL optical goniometer (OEG) and computer software SurfTens 4.5 for analyzing the recorded image of drops. The measurements were carried out at the room temperature ($T = 23 \pm 1 \text{ }^\circ\text{C}$) in 60 seconds with the sampling rate of 1 Hz. The tests were carried out for both the non-coated samples (substrate) and the samples with polymer coatings in the initial state and after 1, 2 and 3-month exposure to the Ringer's solution at $37 \text{ }^\circ\text{C}$.

Resistance to pitting corrosion was tested by the potentiodynamic method, meeting the requirements of PN-EN ISO 10993-15 standard, with the use of PGP201 potentiostat (by Radiometer). The reference electrode was Ag/AgCl 3M KCl electrode, while the auxiliary one was a platinum rod. The scan rate was equal to 3 mV/s. Assays were carried out in Ringer's solution of the following chemical composition: $\text{NaCl} - 8.6 \text{ g/dm}^3$, $\text{KCl} - 0.3 \text{ g/dm}^3$, $\text{CaCl}_2 \cdot 2\text{H}_2\text{O} - 0.33 \text{ g/dm}^3$, at the temperature of $T = 37 \pm 1 \text{ }^\circ\text{C}$ and $\text{pH} = 6.9 \pm 0.2$. The tests were carried out for both the non-coated samples (substrate) and the samples with polymer coatings in the initial state and after 1, 2 and 3-month exposure to the Ringer's solution.

Metal ion concentration in the Ringer's solution after 1, 2 and 3-month exposure was measured with JY 2000 spectrometer by Yobin-Yvon, using inductively coupled plasma-atomic emission spectrometry (ICP-AES). The tests were carried out for both the non-coated and the coated samples.

Tests of adhesion of the polymer coatings to the Ti6Al7Nb substrate were carried out using the scratch test method, using an open platform equipped with a CSM Micro-Combi Tester in accordance with the PN-EN 1071-3 standard. The test consisted of making scratches using a penetrator – a Rockwell diamond cone – with a gradual increase in the normal force loading the penetrator. Due to the diffi-

culty in estimating the critical force L_c using macroscopic observations, a comparison of the obtained F_f friction force for the non-coated and coated samples was proposed. The intersection point of the curves was treated as the force causing delamination of the layer. The tests were carried out with increasing F_c loading force from 0.03 to 30 N and with the following parameters: loading speed $v_s = 10 \text{ N/min}$, table speed $v_t = 1 \text{ mm/min}$, crack length $l = 3 \text{ mm}$. Three measurements were taken on each sample. The tests were carried out for samples in the initial state and after 1, 2 and 3-month exposure to the Ringer's solution at $37 \text{ }^\circ\text{C}$.

3. Results

3.1. Microscopic observations

The surface of the metal substrate was characterized by evenly distributed traces of the sandblasting process carried out (Fig. 1). The polymer coatings applied on the metal substrate with the active substance, regardless of the type of the polymer and their application parameters were characterized by translucency, homogeneity and continuity over the whole surface of the samples (Figs. 2a, 3a, 4a). However, as a result of exposure to Ringer's solution, local discoloration of the coatings was observed. The amount and surface area of discolorations, resulting from the degradation of polymers, increased with the exposure time. The discoloration process was independent of the type of polymer used. In contrast, its severity was observed in coatings obtained as a result of a greater number of dips (Figs. 2b–d, Figs. 3b–d, Figs. 4b–d).

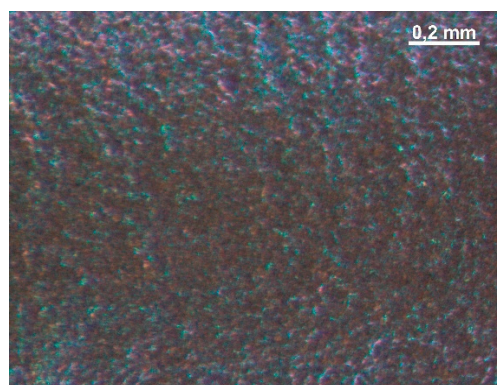


Fig. 1. The surface of the sandblasted and oxidized Ti6Al7Nb alloy

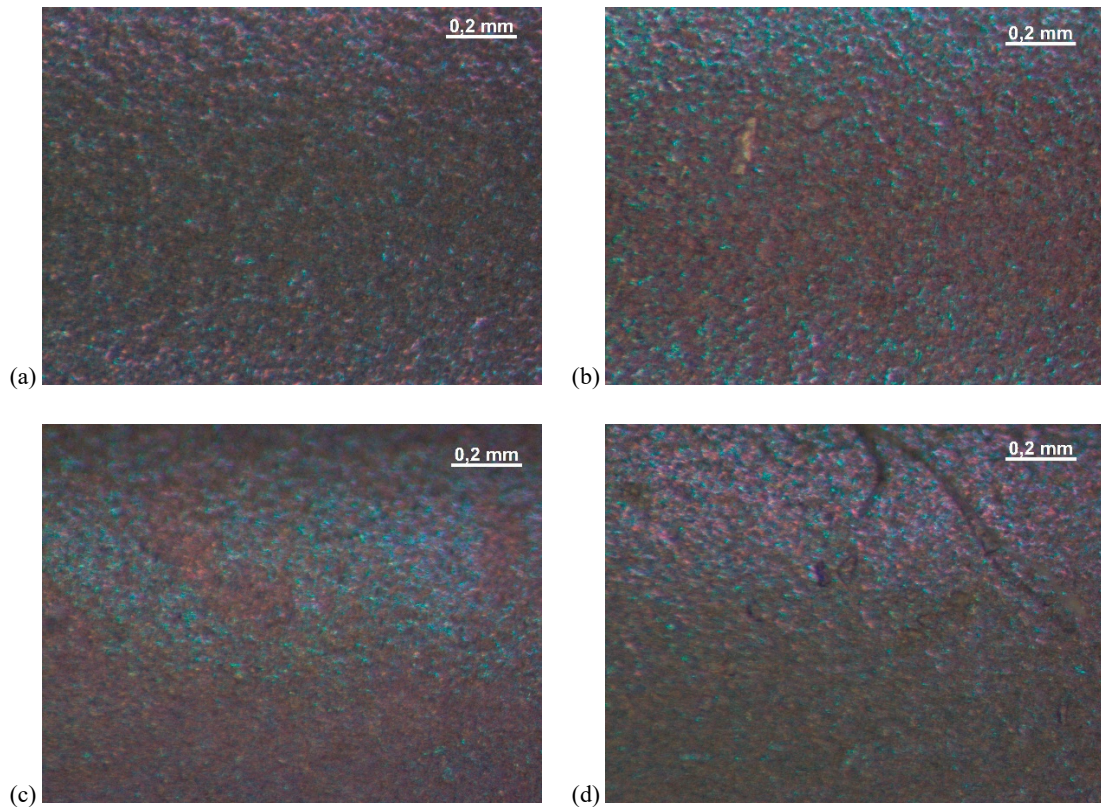


Fig. 2. Surface of the P(L/TMC) polymer coating obtained after one dip: (a) initial state, and after different exposure times to Ringer's solution, (b) 1 month, (c) 2 months, (d) 3 months

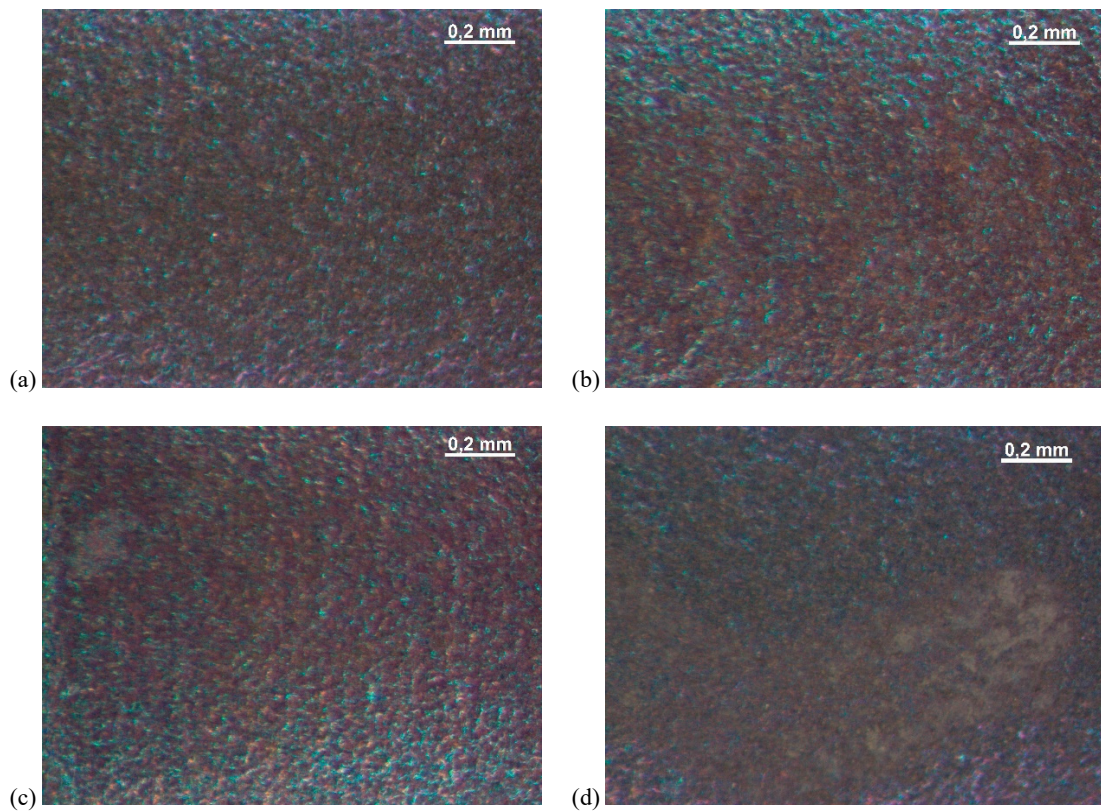


Fig. 3. Surface of the P(L/TMC/G) polymer coating obtained after two dips: (a) initial state, and after different exposure times to Ringer's solution, (b) 1 month, (c) 2 months, (d) 3 months

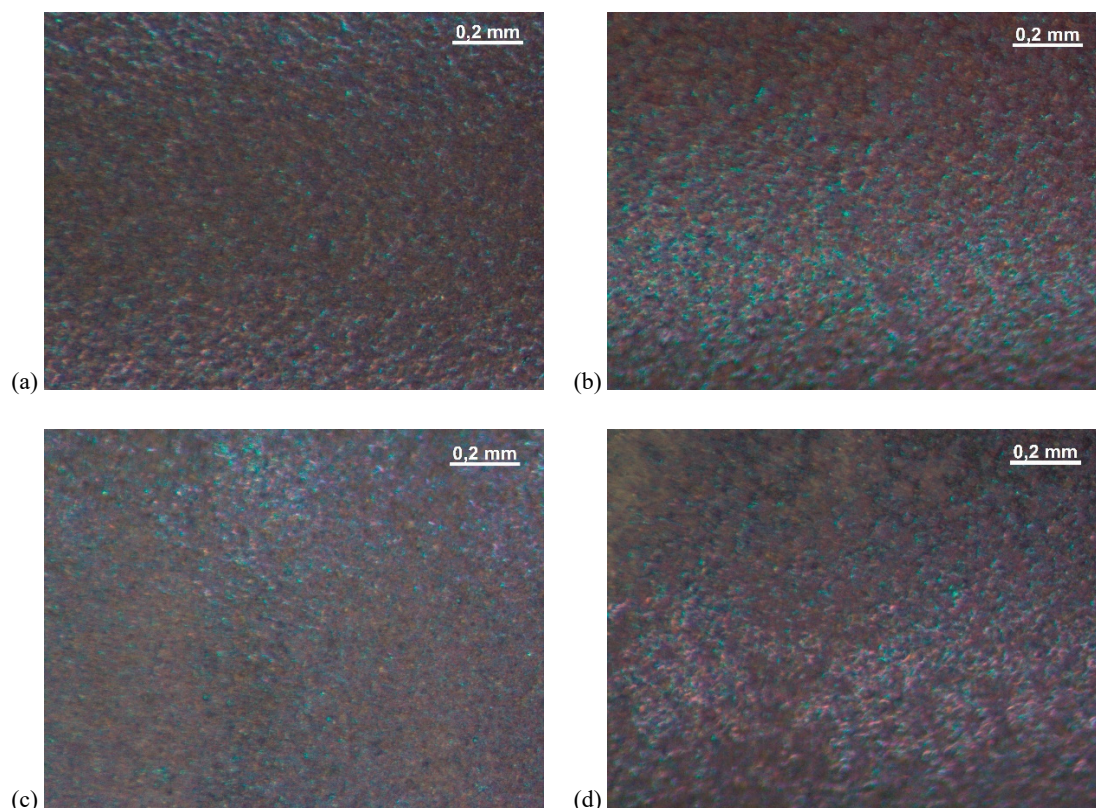


Fig.4. The surface of the PLGA polymer coating obtained after three dips: (a) initial state, and after different exposure times to Ringer's solution, (b) 1 month, (c) 2 months, (d) 3 months

3.2. Surface roughness

The S_a roughness parameter of the polymer coatings obtained after one dip, regardless of the type of polymer, were similar to the roughness of the metal substrate ($S_a = 0.4383 \mu\text{m}$) (Table 1). After a 3-month exposure to Ringer's solution, an increase in surface roughness was observed for most polymers.

Table 1. The roughness of polymer coating

The type of coating	Number of dips	The roughness of the coating S_a [μm]	
		Initial state	After 3 months
P(L/TMC)	1	0.4365	0.3246
	2	0.4101	0.5556
	3	0.3935	0.5168
P(L/TMC/G)	1	0.4121	0.4529
	2	0.3819	0.4502
	3	0.3420	0.3689
PLGA	1	0.4390	0.4853
	2	0.4670	0.5240
	3	0.4488	0.3831

3.3. Wettability

Wettability of the polymer coatings in the initial state was dependent on the type of polymer (Table 2). However, regardless of the polymer used, a decrease in wettability was observed with an increase in the number of dips as a result of which the coating was obtained. Exposure to Ringer's solution increased the wettability of the coatings regardless of their type and number of dips.

3.4. Corrosion resistance

The analysis of the course of the sample polarization curves clearly indicates that the application of polymer coatings to the metal substrate, regardless of their type and application parameters, reduces the current density in the entire measurement range compared to the metal substrate (Fig. 5). With the increase of the exposure time of samples with the polymer coatings, regardless of their type and application parameters, an increase in current density over the entire measurement range was observed compared to the non-exposed samples (Fig. 6). The values of the parameters describing corrosion resistance of the tested samples are summarized in Table 3.

Table 2. Surface wettability of polymer coatings

The type of coating	Number of dips	Contact angle θ [°]			
		0 months	1 month	2 months	3 months
P(L/TMC)	1	66.9 (11)	53.97 (83)	51.83 (84)	37.99 (20)
	2	63.8 (11)	55.23 (13)	52.56 (88)	47.46 (18)
	3	67.52 (40)	53.87 (17)	46.8 (29)	41.71 (91)
P(L/TMC/G)	1	64.2 (21)	49.0 (29)	42.56 (92)	37.68 (10)
	2	73.0 (17)	59.56 (75)	45.85 (18)	38.0 (14)
	3	79.2 (19)	51.92 (39)	52.52 (23)	31.17 (86)
PLGA	1	55.9 (17)	61.82 (92)	52.0 (15)	59.46 (18)
	2	61.29 (62)	53.4 (10)	48.83 (44)	45.58 (58)
	3	66.8 (19)	53.89 (45)	54.83 (23)	43.87 (30)
Ti6Al7Nb		68.7 (21)			

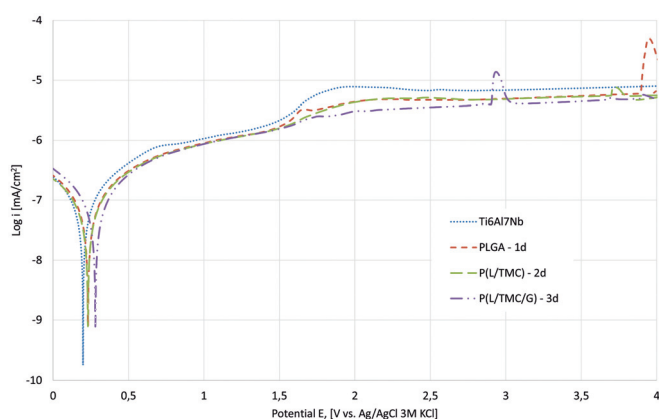


Fig. 5. Polarization curve of Ti6Al7Nb alloy and the alloy coated with polymer coating: PLGA, P(L/TMC), P(L/TMC/G) obtained as a result of different number of dips respectively 1, 2, 3 (initial state)

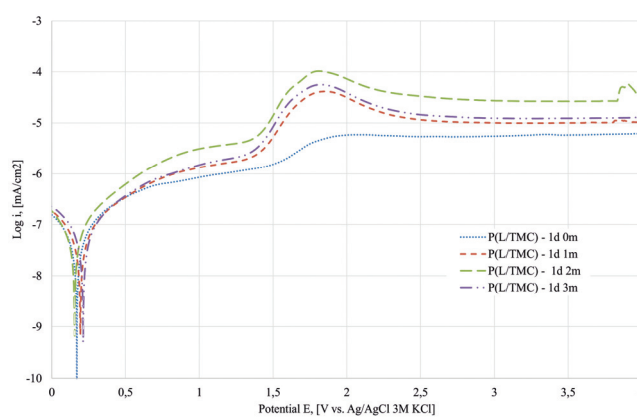


Fig. 6. Polarization curve of Ti6Al7Nb alloy with P(L/TMC) polymer coating obtained as a result of 1 dip in the initial state and after 1, 2 and 3 months exposure to Ringer's solution

For the samples in the initial state with the PLGA and P(L/TMC/G) polymer coatings, regardless of the application parameters, an increase in the corrosion potential of E_{corr} was found in comparison with the metal substrate. In the case of the P(L/TMC) coating in relation to the metal substrate, the E_{corr} corrosion potential decrease was found regardless of the number of dips. In contrast, for all considered variants of polymer coatings, an increase in the R_p polarization resistance value was observed in comparison with the metal substrate. The effect of long-term exposure to Ringer's solution was lowering the value of recorded corrosion potentials both for the metal substrate and coated samples regardless of the type and application parameters. However, no explicit influence of exposure time, type of coating and its application parameters on the value of polarization resistance were found.

3.5. Ion release

The mass density of metallic ions releasing from the surface of the samples coated with biodegradable polymer coatings depends on the type of the polymer, the parameters of its obtaining and exposure time (Table 4). The application of a polymer coating to the metal substrate, regardless of its type and the number of dips, resulted in a reduction in the number of metallic ions releasing to the Ringer's solution in relation to those released from the metal substrate. In addition, it was found that as the number of dips increased, the number of metal ions releasing the Ringer solution decreased. The increase in exposure time resulted in an increase in the amount of released metallic ions.

Table 3. Results of potentiodynamic studies

Exposure time, month	Number of dips	Ti6Al7Nb		+PLGA		+P(L/TMC)		+P(L/TMC/G)	
		E_{corr} [mV]	R_p [$M\Omega \cdot cm^2$]	E_{corr} [mV]	R_p [$M\Omega \cdot cm^2$]	E_{corr} [mV]	R_p [$M\Omega \cdot cm^2$]	E_{corr} [mV]	R_p [$M\Omega \cdot cm^2$]
0	0	162 (61)	0.85 (11)	–	–	–	–	–	–
	1	–	–	240.6 (32)	0.904 (10)	–144 (99)	1.12 (11)	238 (21)	0.81 (10)
	2	–	–	249.35 (78)	0.84 (10)	–94 (54)	1.01 (10)	263 (10)	0.84 (11)
	3	–	–	218 (53)	0.83 (11)	–92.0 (70)	0.98 (10)	281.6 (85)	0.88 (10)
1	0	110 (99)	0.76 (10)	–	–	–	–	–	–
	1	–	–	132 (68)	1.05 (10)	–133 (26)	0.94 (13)	171.3 (32)	0.86 (11)
	2	–	–	195.3 (63)	0.91 (10)	–234 (28)	0.84 (10)	171.6 (21)	0.93 (10)
	3	–	–	166 (39)	0.85 (16)	–212 (32)	0.84 (10)	171 (22)	0.95 (13)
2	0	79 (48)	0.91 (10)	–	–	–	–	–	–
	1	–	–	167.2 (39)	0.98 (10)	–147 (11)	0.79 (10)	151 (11)	0.90 (10)
	2	–	–	145 (16)	0.88 (10)	–102 (74)	0.82 (10)	115 (99)	0.82 (11)
	3	–	–	153 (19)	0.94 (10)	–189 (87)	0.78 (10)	191 (26)	0.82 (10)
3	0	–214.1 (51)	3.02 (91)	–	–	–	–	–	–
	1	–	–	182 (42)	0.87 (10)	–125 (24)	0.92 (11)	250 (25)	0.83 (10)
	2	–	–	239 (13)	0.78 (10)	–129.5 (63)	0.96 (18)	234.1 (52)	0.81 (11)
	3	–	–	223 (39)	0.88 (10)	–189 (17)	0.81 (10)	244.3 (68)	0.84 (12)

Table 4. Results of the surface mass density of metal ions [$\mu g/cm^2$]

The type of coating	No. of dips	The mass density of metallic ions, $\mu g/cm^2$								
		1 month			2 months			3 months		
		Ti	Al	Nb	Ti	Al	Nb	Ti	Al	Nb
P(L/TMC)	1	7.69 (18)	0.963 (18)	5.45 (18)	9.48 (36)	1.091 (36)	5.69 (36)	11.12 (18)	1.455 (45)	5.80 (18)
	2	6.42 (18)	0.609 (18)	5.27 (36)	7.27 (18)	0.736 (18)	5.51 (18)	10.72 (54)	1.163 (54)	5.63 (18)
	3	5.25 (18)	0.391 (18)	3.99 (18)	5.66 (27)	0.618 (36)	4.54 (18)	7.06 (18)	0.872 (36)	5.21 (18)
P(L/TMC/G)	1	5.87 (18)	–	2.05 (36)	7.272 (18)	–	2.85 (36)	8.21 (18)	–	5.60 (18)
	2	4.58 (36)	–	1.72 (45)	5.26 (18)	–	2.81 (90)	5.48 (18)	–	4.60 (27)
	3	3.59 (27)	–	1.51 (36)	3.69 (27)	–	1.94 (45)	4.04 (36)	–	3.63 (18)
PLGA	1	2.81 (18)	–	1,636 (36)	3.61 (27)	–	2.03 (36)	4.05 (55)	–	2.24 (18)
	2	1.79 (36)	–	1.200 (27)	2.11 (54)	–	1.300 (36)	3.01 (54)	–	1.609 (45)
	3	1.473 (45)	–	0.845 (18)	1.764 (18)	–	1.191 (18)	1.872 (18)	–	1.382 (27)
Ti6Al7Nb		22.82 (18)	19.91 (18)	18.14 (18)	23.93 (27)	20.44 (36)	18.2 (27)	24.60 (18)	21.63 (18)	18.4 (18)

3.6. Adhesion of polymer coating

The adhesion of polymer coatings to the metal substrate was dependent on the type of polymer and the method of its obtaining (number of dips) (Table 5). Regardless of the type of polymer for the samples in the initial state, it was observed that with the increase in the number of dips, the adhesion of the coating decreased. After the first month of exposure to the Ringer’s solution, an increase in adhesion forces was observed regardless of the type of polymer and coating parameters. A high value of adhesion force after 2 months of exposure to Ringer’s solution was maintained only for the PLGA coating, for the others a large decrease in the adhesion force was observed. However, 3-month exposure resulted in a decrease in the adhesion of all coatings.

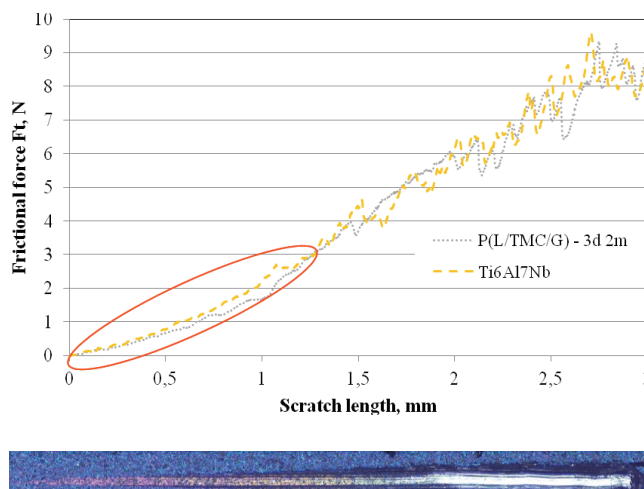


Fig. 7. Example of adhesion test results for the PL/TMC/G polymer coating obtained after three dips

Table 5. Adhesion of the polymer coating to the metal substrate

The type of coating	Number of dips	The force that destroys the sample F_f [N]			
		0 months	1 month	2 months	3 months
P(L/TMC)	1	12.91 (38)	21.54 (42)	1.99 (36)	0.27 (11)
	2	10.34 (49)	11.49 (32)	1.70 (30)	0.18 (10)
	3	7.45 (54)	5.14 (53)	0.62 (19)	0.18 (10)
P(L/TMC/G)	1	15.25 (51)	27.03 (91)	1.75 (29)	0.84 (21)
	2	13.20 (20)	22.90 (69)	0.41 (11)	0.58 (13)
	3	1.69 (36)	5.31 (24)	0.21 (10)	0.18 (10)
PLGA	1	14.00 (29)	15.88 (36)	14.35 (21)	0.58 (14)
	2	9.14 (51)	9.75 (20)	14.09 (35)	0.23 (11)
	3	6.83 (34)	6.32 (54)	14.08 (28)	0.21 (10)

4. Discussion

Analysis of the results of the surface topography of the samples with the polymer coating obtained by a single dip indicates the inheritance of the topography of the metal substrate (Figs. 2a, 3a, 4a). Similar observations were noted by Kazek-Kesik et al. [11]. The increase in the number of dips causes a reduction in coating roughness in the case of P(L/TMC) and P(L/TMC/G) polymers (Table 1). For the PLGA polymer coating, the surface roughness was independent from the number of dips and was maintained at a similar level of roughness of the metal substrate. For most polymer coatings, after 3 months of exposure to Ringer's solution, an increase in surface roughness was observed. This effect is related to the degradation process of polymer coatings exposed to Ringer's solution. The polymer coating applied to the Ti6Al7Nb alloy substrate regardless of the type and application parameters (number of dips) was characterized by continuity, homogeneity and translucency [20]. However, as a result of exposure to Ringer's solution on the coating, local discoloration (transparency reduction) of the coating was observed, what might be connected with the increase of crystallinity induced by degradation, or can be associated with the appearance of oligomers susceptible to crystallization, which is a well-known effect described in the literature [14], [20]. The area of the discoloration increased over time (Figs. 2b–d, Figs. 3b–d, Figs. 4bd). Exposure to Ringer's solution also caused changes in the wettability of the polymer coatings (Table 2). The wettability of polymer coatings increased with the exposure time, which may indicate swelling of the coatings. It can be also connected with the acidic products of the degradation of the polymer chain, which appear on the sur-

face as well as within the material. The process of formation of acidic products during PLA degradation was described in detail by Li S. [15]. Only in the case of the PLGA coating obtained as a result of a single immersion, a similar wettability was observed throughout the exposure period. The application of the polymer coatings, regardless of the type and application parameters, causes a reduction in the current density over the entire measurement range compared to the metal substrate (Fig. 5). This demonstrates good protective properties of the polymer coatings effectively limiting the degradation of the metal substrate. With the time of exposure to Ringer's solution, the recorded current density increased throughout the entire measurement range (Fig. 6). Moreover, in the 1.5 to 2 V potential range for the samples after 1, 2 and 3-month exposure, a distinct increase in the current density was observed [9]. The increase in current density in this potential range is related to the remodelling of the oxide layer on the surface of the Ti alloy. This remodelling indicates the progressive degradation of the polymer coatings, and thus the increasing contact of the metal substrate with the surrounding corrosive environment. The effectiveness of limiting the degradation of the metal substrate by polymer coatings has been confirmed in studies of the concentration of ions releasing into Ringer's solution [9]. Compared to the concentration of metal ions permeating the substrate in the case of polymer coatings regardless of their type as well as the method of obtaining, a reduction in the number of ions was observed (Table 4). Over time, the concentration of ions increased. The use of P(L/TMC/G) and PLGA coatings eliminated the release of Al ions. It is worth noting that the amount of ions released to the solution depends on the number of dips. As the number of dips increases, the concentration of releasing ions decreases. Analysis of the results of the adhesion of polymer coat-

ings to the metal substrate showed that regardless of the type of polymer coating, the highest value was obtained for the coatings after one dip (Table 5). As the number of dips increases, the adhesion force decreases. Exposure to Ringer's solution after the first month results in increased adhesion of the coating. After the second and third month of exposure of the P(L/TMC) and P(L/TMC/G) polymer coatings, the adhesion force dropped significantly. In the case of the PLGA coating, good adhesion of the coating was observed also after the second month. However, after the third month, a clear decrease in the value of the adhesion force was observed.

5. Conclusions

Different kinds of polymers such as: poly(L-lactide-co-trimethylene carbonate) P(L/TMC), poly(L-lactide-co-trimethylene carbonate-glycolide) P(L/TMC/G) and poly(D,L-lactide-glycolide) (PLGA) were used to obtain biodegradable coatings enriched with active substance (ciprofloxacin) formed on Ti6Al7Nb alloy. Developed coatings were characterized by continuity, homogeneity, translucency and good adhesion. However, the adhesion of the coatings in the final stage of the experiment decreased, which was the expected effect, due to biodegradation ability of the coatings. Nevertheless, the study confirmed that the modification of titanium alloy using P(L/TMC), P(L/TMC/G) and PLGA polymer coatings containing ciprofloxacin can constitute a protective barrier limiting degradation processes of the metal substrate. Moreover, the concentration of releasing ions can be further limited by conditions of experiment, i.e., by multiplying the number of dips.

The obtained results indicate the high potential of developed polymeric coatings with biodegradation ability and drug-eluting properties as modified titanium implants.

Acknowledgements

The work is the result of the research project No. 2015/19/B/ST5/03431 funded by the National Science Centre.

References

- [1] BASIAGA M., KAJZER W., WALKE W. et al., *Evaluation of physicochemical properties of surface modified Ti6Al4V and Ti6Al7Nb alloys used for orthopedic implants*, Materials Science and Engineering C – Materials for Biological Applications, 2016, 68, 851–860.
- [2] BULBUL E., AKSAKAL B., *Synthesizing and characterization of nano-graphene oxide-reinforced hydroxyapatite coatings on laser treated Ti6Al4V surfaces*, Acta Bioeng. Biomech., 2017, 19 (4), 171–180.
- [3] GRIJMA D.W., *Poly(trimethylene carbonate) polymers and networks, Synthesis, properties and medical applications*, J. Bioremediat. Biodegrad., 2017, 8 (6), 27.
- [4] JAWORSKA J., JELONEK K., KAJZER W., SZEWCZENKO J., KACZMARCZYK B., MARCINKOWSKI A., JANECZEK H., PASTUSIAK M., BASIAGA M., KASPERCZYK J., *Comparison of biodegradable poly(glycolide-ε-caprolactone) and poly(glycolide-caprolactone-d,l-lactide) coatings enriched with ciprofloxacin formed on Ti6Al4V alloy*, Polym. Degrad. Stab., 2018, 155, 136–144.
- [5] JAWORSKA J., JELONEK K., SOBOTA M., KASPERCZYK J., DOBRZYŃSKI P., MUSIAL-KULIK M., SMOLA-DMOCHOWSKA A., JANECZEK H., JARZĄBEK B., *Shape-memory bioresorbable terpolymer composite with antirestenotic drug*, J. Appl. Polym. Sci., 2015, 132 (17).
- [6] JELONEK K., JAWORSKA J., PASTUSIAK M., SOBOTA M., WŁODARCZYK J., KARPETA-JARZĄBEK P., KACZMARCZYK B., KASPERCZYK J., DOBRZYŃSKI P., *Effect of vascular scaffold composition on release of sirolimus*, European Journal of Pharmaceutics and Biopharmaceutics, 2018, 132, 41–49.
- [7] JELONEK K., KASPERCZYK J., *Polyesters and polyester carbonates for controlled drug delivery*, Part I. Polymers, 2013, 58, 654–662.
- [8] JONES D., *Pharmaceutical Applications of Polymers for Drug Delivery*, Rapra Technology Limited, 2004.
- [9] KAJZER W., JAWORSKA J., JELONEK K., SZEWCZENKO J., KAJZER A., NOWIŃSKA K., HERCOG A., KACZMAREK M., KASPERCZYK J., *Corrosion resistance of Ti6Al4V alloy coated with caprolactone-based biodegradable polymeric coatings*, Eksploatacja i Niezawodność, Maintenance and Reliability, 2018, 20, 130–138.
- [10] KAJZER W., JAWORSKA J., JELONEK K., SZEWCZENKO J., NOWIŃSKA K., KAJZER A., *Effect of sterilization and long-term exposure to artificial urine on corrosion behavior of metallic biomaterials with poly(glicolide-co-caprolactone) coatings*, [in:] M. Gzik, E. Tkacz, Z. Paszczena, E. Piętko (Eds.), *Innovations in biomedical engineering*, Springer International Publishing. Innovations in Biomedical Engineering, 2018, 391–398.
- [11] KAZEK-KĘSIK A., NOSOL A., PŁONKA J., ŚMIGA-MATUSZOWICZ M., GOLDA-CĘPA M., KROK-BORKOWICZ M., BRZYCHCZY-WŁOCH M., PAMUŁA E., SIMKA W., *PLGA-amoxicillin-loaded layer formed on anodized Ti alloy as a hybrid material for dental implant applications*, Materials Science and Engineering C, 2019, 94, 998–1008.
- [12] KIEL M., SZEWCZENKO J., MARCINIAK J., NOWIŃSKA K., *Electrochemical properties of Ti-6Al-4V ELI alloy after anodization*, [in:] E. Piętko, J. Kawa (Eds.), *Lecture Notes in Computer Science, Lecture Notes in Bioinformatics*, Springer, 2012, 7339, 369–378.
- [13] KIEL-JAMROZIK M., SZEWCZENKO J., BASIAGA M., NOWIŃSKA K., *Technological capabilities of surface layers formation on implant made of Ti-6Al-4V ELI alloy*, Acta Bioeng. Biomech., 2015, 17(1), 31–37.
- [14] LI S., VERT G.M., *Structure-property relationship in the case of the degradation of massive poly(α-hydroxyacids) in aqueous media*, Journal of Materials Science, Materials in Medicine, 1990, 1, 131–139.
- [15] LI S., VERT G.M., *Structure-property relationship in the case of the degradation of massive poly(α-hydroxyacids) in aqueous*

- media*, Journal of Materials Science, Materials in Medicine, 1990, 1, 123–130.
- [16] NIINOMI M., *Metallic biomaterials*, J. Artif. Organs., 2008, 11, 105–110.
- [17] POSADOWSKA U., BRZYCHCZY-WŁOCH A., PAMUŁA E., *Gentamicin loaded PLGA nanoparticles as local drug delivery system for the osteomyelitis treatment*, Acta Bioeng. Biomech., 2015, 17 (3).
- [18] PRAKASAM M., LOCS J., SALMA-ANCANE K. et al., *Biodegradable Materials and Metallic Implants. A Review*, Journal of Functional Biomaterials. 8, 4 (2017) 12.
- [19] DOBRZYNSKI P., KASPERCZYK J., *Synthetic biodegradable medical polyesters: Poly(trimethylene carbonate) in Science and Principles of Biodegradable and Bioresorbable*, Medical Polymers Materials and Properties, 2017, 107–152.
- [20] SEAL B.L., OTERO T.C., *Polymeric biomaterials for tissue and organ regeneration*, Mater. Sci. Eng. R. Rep., 2001, 34, 147.
- [21] SZEWCZENKO J., KAJZER W., GRYGIEL-PRADEŁOK M., JAWORSKA J., JELONEK K., NOWIŃSKA K., GAWLICZEK M., LIBERA M., MARCINKOWSKI A., KASPERCZYK J., *Corrosion resistance of PLGA-coated biomaterials*, Acta Bioeng. Biomech., 2017, 19, 1, 173–179.
- [22] SZEWCZENKO J., MARCINIAK J., TYRLIK-HELD J., NOWIŃSKA K., *Effect of surface pretreatment on corrosion resistance of anodically oxidized Ti6Al7Nb alloy*, [in:] E. Piętko, J. Kawa (Eds.), *Lecture Notes in Computer Science*, Vol. *Lecture Notes in Bioinformatics*. Springer, 2012, 7339, 398–411.
- [23] SZEWCZENKO J., NOWIŃSKA K., MARCINIAK J., *Influence of initial surface treatment on corrosion resistance of Ti6Al4V ELI alloy after anodizing*, Przegląd Elektrotechniczny, 2011, 87, 228–231.
- [24] TUREK A., KASPERCZYK J., JELONEK K., BORECKA A., JANECZEK H., LIBERA M., GRUCLIK A., DOBRZYŃSKI P., *Thermal properties and morphology changes in degradation process of poly(lactide-co-glycolide) matrices with risperidone*, Acta Bioeng. Biomech., 2015, 17 (1).
- [25] WANG M., *Surface Modification of Metallic Biomaterials for Orthopaedic Applications*, Materials Science Forum, 2009, 618, 619, 285–290.
- [26] WEN C., *Surface Coating and Modification of Metallic Biomaterials*, Elsevier, 2015.
- [27] ZHANG Z., GRIJPMAN D.W., FEJEN J., *Creep-resistant porous structures based on stereocomplex forming triblock copolymers of 1,3-trimethylene carbonate and lactides*, Journal of Materials Science, Materials in Medicine, 2004, 15, 381–385.