Impact of Surface Topography, Chemistry and Properties on the Adhesion of Sodium Alginate Coatings Electrophoretically Deposited on Titanium Biomaterials

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In this paper, we report on the electrophoretic deposition and characterisation of pure sodium alginate coatings on titanium biomaterials, the commercially pure titanium CP-Ti1 and Ti–13Nb–13Zr titanium alloy. Various solutions differing in the distilled water to ethanol volume ratio and sodium alginate concentration were used for coating deposition. Uniform, dense and continuous coatings with a thickness up to 1 μm were deposited. The effect of surface topography and morphology, wettability and surface free energy as well as surface chemistry on the coating adhesion to the titanium biomaterials were investigated. The coatings exhibited very good adhesion to the polished and then chemically treated alloy. The adhesion mechanisms were identified. The chemical bonding and interfacial adhesion mechanisms are plausible. The coatings exhibited low surface development, dependent on the applied substrate roughness. Sodium alginate coatings on both substrates showed moderate hydrophilicity and relatively high surface free energy, on average 30 pct higher in comparison with that of the substrate materials. The obtained results will be useful for the further development of composite sodium alginate coatings for enhancing the biological performance of titanium biomaterials.

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I. INTRODUCTION

TITANIUM and titanium alloys are important metallic materials in biomedical engineering due to their unique properties. They have a high specific strength, excellent electrochemical corrosion resistance, relatively low elastic modulus, low density and good biocompatibility. These materials are often used in orthopaedic surgery and traumatology as well as in dentistry, mainly for bone implants.\[^{1,2}\] On the other hand, the biomedical applications of Ti and its alloys are limited by their poor bioactivity. They are considered as bioinert to the human body.\[^{3}\] To improve their biological properties, polymer, ceramic or composite coatings are often applied.\[^{4-8}\] One of the natural biopolymers with great potential is alginate. It is a biodegradable, high biocompatible, low cost and non-toxic anionic polymer, commonly extracted from brown algae.\[^{9-12}\] This polymer is widely used for many medical applications, for instance, drug delivery, nerve tissue repair or wound dressing\[^{13-16}\] and for biomedical coatings.\[^{17-19}\] A beneficial technique for the deposition of alginate coatings on conducting materials is electrophoretic deposition (EPD).\[^{15,17,18,20-22}\] In this process, charged particles dispersed in the dispersion phase move to a conductive substrate of opposite charge under the electric field to obtain a coating.\[^{17,21,23}\] EPD has many advantages, such as room temperature processing, a short deposition time and uncomplicated control of process parameters. The EPD of pure sodium alginate coatings on the Ti–15Mo titanium alloy was previously reported, in particular by Szklarska et al.\[^{15}\] They found that the morphology of the coating can be easily controlled by voltage and deposition time. A porous coating was obtained at a voltage of 50 V, as a result of an evolution of oxygen at the anode. Deposition at lower voltages led to dense coatings being obtained. However, the adhesion of the coatings to the alloy was not considered in that work. Sodium alginate has been widely used as the matrix of composite coatings electrophoretically deposited on titanium substrates,\[^{20}\] titanium alloy substrates,\[^{24}\] stainless steel substrates\[^{17,18}\] or magnesium alloy substrates.\[^{25}\] Those
papers describe the EPD route of composite coatings and selected properties. In our previous work,\cite{20} we used the sodium alginate (SA) concentration of 4 g/L in the suspension as well as different concentrations of hydroxyapatite (HA) particles and the volume ratio of distilled water to ethanol 60/40 to avoid hydrogen evolution during the process. It was found that the homogeneity of the fabricated coatings depended largely on the chemical composition of the suspension, whereas their adhesion depended significantly on the surface substrate preparation. The coatings exhibited poor adhesion to the as-received titanium and high adhesion to the chemically-treated substrates. Zhitomirsky \textit{et al.}\cite{10} used a suspension containing SA with a concentration of 0.5 g/L and a different concentration of ceramic particles (Bioglass and HA) to deposit composite coatings. They found that the thickness of the coatings was not uniform and was determined by the contents of ceramic particles in the suspension. Sridevi \textit{et al.}\cite{24} used a solution of ethanol and water in the ratio of 1:2 and the concentration of SA 1, 2 and 3 wt pct to develop carboxymethyl cellulose/sodium alginate coatings. The pH of all solutions was modified to reach 7. The obtained coatings exhibited very good mechanical and antibacterial properties but up to the concentration of SA in the solution equal to 2 wt pct. Higher SA concentrations in the solution decreased the apatite layer formation during the biomineralization process as well as mechanical and antibacterial properties. The authors also reported that the homogeneity of fabricated coatings must be improved to eliminate localised corrosion. Cordero-Arias \textit{et al.} developed composite ZnO/alginate and ZnO-bioactive glass/alginate\cite{17} and TiO$_2$/alginat\cite{22} coatings. They used a solution of SA with a concentration of 2 g/L and 60/40 volume ratio of distilled water to ethanol to avoid hydrogen evolution during EPD. It was found that the EPD process was driven by the mobility of the alginate molecules because the ‘polymer cloud’ containing ceramic particles moved to the electrode and formed a composite coating.\cite{17} Interestingly, to avoid possible cracks in the TiO$_2$/ alginate coatings, the samples were soaked (3 times during 1 minute) in a solution containing 2 wt pct of SA in water.\cite{25} Nevertheless, the coatings included micro-cracks all over the surface, probably due to hydrogen evolution during the EPD process or as a result of shrinkage of the coating during the drying process. The coatings were not peeled off from the magnesium alloy after the adhesion test and exhibited better corrosion resistance compared with uncoated substrates. To summarise the literature review, there is one paper on the EPD of pure sodium alginate coatings and several papers about the EPD of composite coatings with an SA matrix. However, these papers contain little information about the adhesion of coatings to metallic substrates and no information about the influence of the substrate preparation before the deposition on the coating adhesion. It is well known\cite{20,25–31} that the adhesion of the coating to an underlying material is beneficial from the application point of view of the coated material. It depends on the durability of the coating/substrate system and is highly dependent on the surface condition of the base material\cite{26}. The adhesion of coatings to metallic substrates is a complex phenomenon that depends on various factors, such as chemical and phase composition of the substrate, surface roughness and topography, surface free energy and wettability, surface charge, and substrate purity or the presence of defects.\cite{27–31} Besides this, the physical properties of both the substrate and coating materials are of great importance, particularly the thermal and elastic mismatch between the coating and the substrate and the coating thickness.\cite{26} Thus, the excellent organic sodium alginate coating adhesion should be foreseen from both optimised chemistry enabling covalent bonding of the coating to the titanium substrates and surface topography features enabling mechanical interlocking of the coating.

The aim of the present work was (i) to deposit homogeneous pure sodium alginate coatings on various titanium biomaterials, such as the commercially pure titanium and Ti–13Nb–13Zr titanium alloy substrates, (ii) to investigate the influence of substrate preparation (surface features, roughness, wettability and chemistry) on the adhesion of the coating, as well as (iii) to investigate the microstructure of the coating, and effect of the coating on surface topography and surface properties, wettability and surface free energy, of the titanium biomaterials.

\section{EXPERIMENTAL}

\subsection{Substrate Materials}

The commercially pure titanium Grade 1 (CP-Ti1) and Ti–13Nb–13Zr titanium alloy were used as substrates for coatings. The titanium substrates were delivered in the as-rolled condition by Shanghai Industry Co. Ltd, China. The titanium alloy was provided by Xi’an Saite Metal Materials Development Co., Ltd., China. The CP-Ti1 samples had the shape of a plate with the dimension of 30 mm $\times$ 15 mm and a thickness of 0.5 mm. The titanium alloy samples had the shape of discs with a diameter of 30 mm and the thickness of approx. 2 mm. The microstructure of the materials has been described elsewhere, for titanium\cite{30,32} and the alloy.\cite{33,34}

Different routes of substrate preparation were used: CP-Ti1 \textit{Type 1 substrates} were used in the as-received condition. They were washed with distilled water and ethanol directly before the EPD. The \textit{alloy Type 1 substrates} were ground with a successively finer grit of sandpaper up to 3000-grit and, in the end, mechanically polished with the use of a colloidal silica suspension (Struers, the grain size of 0.25 $\mu$m). CP-Ti1 \textit{Type 2} and polished Ti alloy \textit{Type 2 substrates} were washed in acetone and then soaked in a 0.06 M solution of Na$_3$PO$_4$ $\cdot$12H$_2$O at a temperature of 80 $^\circ$C. Afterwards, they were washed in hot water and soaked in a solution consisting of 5 mL HF 40 pct + 35 mL HNO$_3$ 70 pct in 60 mL H$_2$O for 5 minutes, as described elsewhere.\cite{30,35}

Besides this, in the case of CP-Ti1, other treatments were also applied.
The citric acid (C\textsubscript{6}H\textsubscript{8}O\textsubscript{6}) and sodium hydroxide (NaOH) were used to change the pH of the solutions. Citric acid, 99 pct pure, anhydrous, was supplied by ACROS Organics (Belgium) and the NaOH micro pills were supplied by Avantor Performance Materials Poland S.A.

B. EPD of Coatings

The synthetic SA powder (no. W201502) was delivered by Sigma-Aldrich. Solutions for coating deposition were prepared with a different concentration of SA powder (2, 4 or 8 g/L) and a different volume ratio of distilled water to ethanol (purity 99.8 pct), which equalled 20/80, 40/60 or 60/40 vol pct. A total solution volume of 50 mL was always maintained. SA was dissolved in distilled water for 10 minutes while being magnetically stirred at 600 rpm. Then the solution was ultrasonically dispersed at room temperature (RT) for 10 minutes and ethanol was slowly added during continuous stirring at 600 rpm. Directly before the EPD process, the suspension was once more magnetically stirred at 600 rpm for 5 minutes. EPD was performed at the constant voltage of 3, 5, 7, 10 and 12 V for a deposition time of 1 and 5 minutes. The constant voltage was applied using an EX752M Multi-mode PSU standard.

C. Characterisation of Microstructure and Surface Topography

The microstructure of the substrate materials and selected coatings was characterised by scanning electron microscopy (SEM) using a FEI NovaSEM 450 (the Netherlands). The selected coatings were also investigated by transmission electron microscopy (TEM) using a JEM-2010 ARP microscope of JEOL (Japan). The phase composition was investigated by grazing incidence X-ray diffractometry (GIXRD) using a Panalytical Empyrean DY1061 diffractometer (the Netherlands) and by selected area electron diffraction (SAED).

X-ray Photoelectron Spectroscopy (XPS) was applied to determine the oxidation state of the metallic elements on the surface of the CP-Ti1 Type 1, CP-Ti1 Type 2 and Ti alloy Type 1 and Type 2 substrates. The XPS spectrometer was produced by VSW (Vacuum System Workshop Ltd., UK). The radiation of the Mg X-ray lamp (Mg K\textsubscript{\alpha} photon energy equal to 1253.6 eV) was applied to induce the photoemission process. Photoelectrons energy was analysed in a hemispherical analyzer using the fixed-analyse transition mode with the pass energy of electrons equal to 22 eV. Calibration of the binding energy scale was performed by assuming that the position of the C 1s line of the adventitious carbon, corresponding to the C–H bond, is equal to 284.6 eV.

The surface topography of the coatings was analysed with a WYKO NT930 optical profilometer. To obtain surface images, scanning areas of 1.3 mm \(\times\) 0.9 mm were used.

D. Characterisation of Coating Adhesion and Surface Properties

The adhesion of the coatings to the substrates was investigated by a cross-cut adhesion test using a cutting knife from Elcometer for coatings on metals and a special tape in accordance with ASTM D3359B. A cut mesh was made on the coating and then the tape was glued. After 90 seconds the tape was peeled off. The surface of the samples was observed by light microscopy (LM) and SEM. The area removed was measured with the use of ImageJ software and compared with the table of adhesion test results from the ASTM D3359B standard.

The contact angle and surface free energy (SFE) of the substrates and coatings was investigated using a Krüss DSA25E goniometer (Germany). Two different solutions of diiodo-methane (CH\textsubscript{2}I\textsubscript{2}) as a non-polar liquid and pure water (H\textsubscript{2}O) as a polar liquid were used. SFE was calculated using the Owen–Wendt–Rabel–Kaelble (OWRK) method as a sum of polar and dispersive component results.

III. RESULT AND DISCUSSION

A. EPD of Coatings

Several papers on the EPD of alginites as a matrix of coatings have been reported\textsuperscript{[17,18,39,40]} in these previous papers, the authors used only one solution with the volume ratio of distilled water to ethanol equal to 60/40 and these studies provide no data about the influence of different volume ratios of distilled water to ethanol on the solution stability, e.g. precipitation of sodium alginate. Various solutions with different volume ratios...
of distilled water to ethanol and different concentrations of SA, presented in Table I, were investigated to elaborate a stable solution and to deposit homogeneous and reproducible coatings in the present work. It could be seen with the naked eye that a stable solution was obtained for the distilled water to ethanol volume ratio equal to 60/40 and SA equal to 2, 4, or 8 g/L with a value of pH 6.80, 6.70, 6.35, respectively (solutions 7 to 9 in Table I). In the case of the dispersion phase consisting of a distilled water to ethanol volume ratio of 20/80 or 40/60, the precipitation of SA was observed for all investigated solutions with the concentration of SA equal to 2, 4 and 8 g/L (solutions 1 to 3 and 4 to 6, respectively). The precipitation was the highest for the solution containing the volume ratio of distilled water to ethanol of 20/80 and slightly lower for the solution containing the volume ratio of distilled water to ethanol of 40/60. The precipitation increased with an increased amount of ethanol in the solution. It is well known\cite{17,20,25,40} that sodium alginate is water-soluble and insoluble in ethanol.

To obtain reproducible and homogeneous coatings the suspension must be stable\cite{41}. The stability of the suspension can be defined by determining the electrokinetic properties of particles in the solution, in particular, the electrophoretic mobility and zeta potential.\cite{33,42} Vallar et al.\cite{43} found that if the zeta potential was higher than ±30 mV then the solution used for EPD was stable. Hence, the stability of the solution in this work was evaluated based on macroscopic observation, taking into account whether there was sodium alginate precipitation as well as pH and zeta potential measurements. Zeta potential of the real solutions incorporating distilled water and ethanol in the vol pct of 60/40 and different contents of SA equal to 2, 4 or 8 g/L (solutions 7 to 9 in Table I) was measured as a function of pH. It was found that the zeta potential exhibited negative values in all solutions in the entire investigated pH range of 3 to 12 and reached high values in solutions with a pH higher than 5 (Figure 1). The highest values of zeta potential for different concentrations of SA equal to 2, 4 and 8 g/L were—56.1, —66.0 and —90.6 mV at pH 6.80, 6.70 and 6.35, respectively. The negative zeta potential means that the SA was negatively charged and deposited on the positive electrode (anode). It was also observed that the instability of the zeta potential value increased with the increase of SA content in the solution and the solution with 8 g/L SA was the most unstable.

The EPD mechanism of sodium alginate (AlgNa) is well known and described elsewhere.\cite{18,21,22} The alginate is soluble in water at a pH higher than 3 and the dissociation of SA in aqueous solutions at a pH range of 3 to 9 leads to the formation of Alg− species according to reaction [1].

\[
\text{AlgNa} \rightarrow \text{Alg}^- + \text{Na}^+ \tag{1}
\]

As a result of the electrochemical decomposition of water [2], the pH value drops at the anode surface.

\[
2\text{H}_2\text{O} \rightarrow \text{O}_2 + 4\text{H}^+ + 4\text{e}^- \tag{2}
\]

Alginate solutions form gels at a pH lower than 3\cite{21} therefore the anionic Alg− macromolecules move towards the anode and, at this lower pH, a water-insoluble coating is formed on it [3].

\[
\text{Alg}^- + \text{H}^+ = \text{AlgH} \tag{3}
\]

Trial series of coatings were deposited from solutions 7 (pH 6.80), 8 (pH 6.70) and 9 (pH 6.35) at different voltages and a constant deposition time of 5 minutes on the CP-Ti1 Type 2 substrates. Figure 2 shows macroscopic images of the coatings deposited from solution 8 at different voltage values and a constant time of deposition. The macroscopically homogeneous coating was obtained at 10 V during 5 minutes (Figure 2(d)). It was observed that the coatings deposited at 3 V and 5 V were not homogeneous due to their non-uniform thickness (Figures 2(a) and (b)). The coating deposited at 7 V was relatively homogeneous but very thin (Figure 2(c)). The higher voltage value (12 V) used during EPD led to the evolution of gas bubbles and the substrates were oxidised (Figure 2(e)). The formation of gas bubbles on the electrode during the EPD process might be explained by the electrolysis of water under the effect of an electric field, which decomposes water into hydrogen and oxygen.\cite{33,40,42} This phenomenon intensifies with increasing voltage during deposition.\cite{42}

The coatings deposited from the solution incorporating 2 g/L SA (solution 7) were not reproducible, very thin and usually only partially coated the substrate. This

| Table I. Chemical Composition, pH and Information About the Precipitation of SA in the Solutions Used for EPD |
| --- |
| No | Sodium Alginate, g/L | Distilled Water to Ethanol, Volume Ratio | pH Value | Precipitation of SA in the Solution |
| --- | --- | --- | --- | --- |
| 1 | 2 | 20/80 | 8.20 | yes (small) |
| 2 | 4 | 8.10 | yes (medium) |
| 3 | 8 | 7.85 | yes (large) |
| 4 | 2 | 7.95 | yes (small) |
| 5 | 4 | 7.86 | yes (medium) |
| 6 | 8 | 7.78 | yes (large) |
| 7 | 2 | 6.80 | no |
| 8 | 4 | 6.70 | no |
| 9 | 8 | 6.35 | no |

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indicates that the SA content in the solution was too low. In contrast, the coatings obtained from the solution with the higher concentration of SA equal to 8 g/L were thick but not homogeneous and the titanium substrates oxidised very quickly. The coatings deposited at a shorter time, e.g., 1 minute, were very thin for all solutions, independent of SA concentration.

The SEM observation of the morphology of coatings deposited from solutions 7, 8, and 9 at the voltage of 10 V for 5 minutes showed that they reflected the surface of the substrates (Figures 3(a) through (c)).

It was also confirmed that the coating obtained from solution 8 was uniform and continuous, with the occasional presence of small precipitates (Figure 3(b)). In contrast, large bubbles with an equivalent circle diameter (ECD) even up to 120 μm occurred in the coating deposited from solutions 7 (Figure 3(a)) and 9 (Figure 3(c)). Moreover, a higher number of precipitates were formed in the coating obtained from solution 9.

In the case of the alloy, uniform, continuous and transparent coatings that allowed the observation of the surface of the substrate were also obtained from solution 8 at a voltage of 10 V during 5 minutes (Figure 4). Therefore, this solution and the EPD processing parameters, the voltage of 10 V and deposition time of 5 minutes, were ultimately selected for the deposition of uniform and robust coatings.

![Zeta potential for solutions containing 2, 4 or 8 g/L SA, distilled water and ethanol in the vol pct of 60/40.](image1)

![Macroscopic images of SA coatings deposited on CP-Ti1 Type 2 from colloidal solution 8 at the voltage of 3 V (a), 5 V (b), 7 V (c), 10 V (d), 12 V (e) and a constant deposition time of 5 min.](image2)

![Morphology of SA coatings on the CP-Ti1 Type 2 substrates obtained from solutions 7 (a), 8 (b) and 9 (c) at the voltage of 10 V and a constant deposition time of 5 min, SEM.](image3)

![Morphology of the SA coating deposited on the alloy Type 2 substrate from solution 8 at the voltage of 10 V and time of 5 min, SEM.](image4)
B. Influence of the Surface Morphology, Topography, Chemistry and Properties on the Coating Adhesion to the Substrates

It was established that the surface preparation of the titanium biomaterials had an essential influence on the adhesion of the coatings. To obtain outstanding coating adhesion, various substrate preparations, described in detail in the experimental section, were applied. The adhesion of the coatings to the CP-Ti1 Type 1, 3 to 5 substrates was very poor (class 0B, according to ASTM B3359B). The entire coating was easily removed during the adhesion tape test (Figure 5(a)). These results were obtained regardless of the coating thickness (deposition time of 1 or 5 minutes). The coatings exhibited higher adhesion to the CP-Ti1 Type 2 substrate (class 2B) (Figure 5(b)). The adhesion of the coating to the alloy Type 1 (alloy with a smooth, polished surface) was also very poor, adhesion class 0B (Figure 5(c)). Surprisingly, high adhesion (class 4B) was exhibited by the coatings to the alloy Type 2 substrates (Figure 5(d)). Small flakes of the coating detached at the cuts accounted for less than 5 pct of the area, indicating class 4B according to ASTM B3359B.

To explain the differences in adhesion of the coatings to the various substrates, the surface morphology and topography, chemistry, and surface properties, such as wettability and SFE, an investigation was performed. SEM observation showed that the as-delivered CP-Ti1 (Type 1) substrate surface contained deep scratches parallel to each other and burrs (Figure 6(a)). The scratches disappeared in the CP-Ti1 Type 2 surface and, instead, open pores with a size up to 6 μm and short microcracks appeared on the surface (Figure 6(b)). The CP-Ti1 Type 3 exhibited smoother surface morphology than the CP-Ti1 Type 1, but scratches could be noticed (Figure 6(c)). Moreover, short microcracks occurred in the surface oxide layer (indicated by arrows in Figure 6(c)). The CP-Ti1 Type 4 was well developed with the presence of open pores on its surface (Figure 6(d)). The CP-Ti1 Type 5 showed a similar surface to the CP-Ti1 Type 3, but there were fewer microcracks (Figure 6(e)).

In the case of the alloy Type 2, which was chemically treated in the same way as the CP Ti1 Type 2 samples, open porosity was not observed on the surface and the surface was very smooth and a fine acicular martensitic morphology composed mainly of α′ were clearly visible (Figure 6(f)). This indicates that both the chemical composition of the material and the state of the sample surface, scratched for CP Ti1 and mirror polished for the alloy, can influence the chemical treatment process.

The surfaces of titanium biomaterials to which the coating showed the greatest adhesion (CP-Ti1 Type 2 and alloy Type 2), as well as those to which the adhesion was poor (e.g. CP-Ti1 Type 1, 3 to 5 and alloy Type 1),
were subjected to surface topography studies using optical profilometry. The typical images of the CP-Ti Type 1 and Type 2, as well as the alloy Type 1 and Type 2 surfaces, are shown in Figures 7(a) through (d). Table II shows roughness parameters, the average roughness ($R_a$), the root mean square roughness ($R_q$) and the maximum vertical distance between the highest and lowest points in the image ($R_t$).

It was found that all investigated CP-Ti1 substrates were characterised by relatively poor surface development. Titanium substrates, CP-Ti1 Type 1, 2 and 5 exhibited similar $R_q$ and $R_a$ parameters, but the scratches in the CP-Ti1 Type 1 sample were much deeper ($R_t = 15.0 \pm 5.3 \mu m$) than the surface features (open pores, scratches, microcracks) in the CP-Ti1 Type 2 to 5 samples. In comparison, CP-Ti1 Type 3 showed higher $R_q$ and $R_a$ parameters, while CP-Ti1 Type 4 present lower $R_q$ and $R_a$ parameters. Both investigated alloy substrates revealed even less roughness, which is due to the polishing of the samples. The applied chemical treatment affects the development of the alloy surface. The $R_a$ and $R_q$ parameters were about twice as high after the treatment. The above results of surface roughness showed that it has no or very little effect on the adhesion of alginate coatings to titanium biomaterials.

The surface chemistry of the CP Ti1 Type 1 and Type 2, as well as the alloy Type 1 and Type 2, were investigated in detail using the XPS method. Figure 8 presents the spectra of the Ti 2p line determined for the CP-Ti1 Type 1 and Type 2 substrates. The spectrum of the former shows only one oxidation state of titanium Ti$^{4+}$ (Ti 2p$_{3/2}$ line at 458.2 eV), while that of the latter shows three oxidation states, Ti$^{4+}$, Ti$^{2+}$ (at 455.8 eV) and Ti$^0$, which is a metallic state (at 453.4 eV). As the probing depth of the XPS method is just a dozen nanometres, because it is equal at maximum to three times the mean free path of electrons, it is clear that the oxide layer thickness on the as-received substrate is greater than this length. Contrary, because of the clearly visible signal from the metallic substrate, the oxide layer thickness on the chemically treated substrate is much lower.

Table II. The Roughness Parameters of the CP-Ti1 Type 1-5 and the Alloy Type 1 and Type 2 Substrates

| Material       | $R_q$ [$\mu m$] | $R_a$ [$\mu m$] | $R_t$ [$\mu m$] |
|----------------|-----------------|-----------------|-----------------|
| CP-Ti1 Type 1  | 0.65 ± 0.10     | 0.42 ± 0.05     | 15.0 ± 5.3      |
| CP-Ti1 Type 2  | 0.65 ± 0.12     | 0.45 ± 0.06     | 6.3 ± 1.2       |
| CP-Ti1 Type 3  | 0.71 ± 0.07     | 0.51 ± 0.03     | 9.0 ± 1.5       |
| CP-Ti1 Type 4  | 0.57 ± 0.01     | 0.44 ± 0.01     | 6.6 ± 1.1       |
| CP-Ti1 Type 5  | 0.64 ± 0.11     | 0.46 ± 0.04     | 8.4 ± 1.7       |
| Alloy Type 1   | 0.11 ± 0.01     | 0.08 ± 0.01     | 2.3 ± 1.9       |
| Alloy Type 2   | 0.26 ± 0.02     | 0.20 ± 0.01     | 3.2 ± 0.5       |

The parameters were obtained from optical profilometry measurements.

![Fig. 7—Typical optical profilometry images of surface topography of the CP-Ti1 Type 1 (a) and Type 2 (b) as well as the alloy Type 1 (c) and alloy Type 2 (d) substrates used for the EPD process.](image-url)
The XPS analysis for the Ti–13Nb–13Zr alloy substrates are presented in Figure 9. The Ti 2p spectra (Figure 9(a)) show that the alloy has three oxidation states, +4, +2 and 0, for the titanium alloy polished substrate (Type 1) as well as titanium alloy substrate after chemical treatment (Type 2). The corresponding positions of the spectral lines are very similar to those shown in Figure 8. The Zr 3d spectra (Figure 9(b)) show two degrees of zirconium oxidation, Zr$^{4+}$ (3d_{5/2} line at 182.5 eV) and Zr$^{0}$ (at 178.1 eV), for the alloy Type 1 and Type 2 substrates. In the case of both titanium and zirconium, the spectral lines corresponding to the lower oxidation states are much weaker than the lines corresponding to the highest oxidation state of these elements. Some differences in the chemical states of the alloy Type 1 and Type 2 substrates can be seen with niobium. The Nb 3d spectra presented in Figure 9(c) reveal that in the alloy Type 1 substrate niobium exhibits 4 oxidation states, Nb$^{5+}$ (3d_{5/2} line at 207.0 eV), Nb$^{4+}$ (at 205.1 eV), Nb$^{3+}$ (at 203.3 eV) and Nb$^{0}$ (at 201.8 eV), but the alloy Type 2 substrate has only three oxidation states, Nb$^{5+}$, Nb$^{4+}$ and Nb$^{0}$. Again, the lines corresponding to the highest oxidation state are by far the strongest. Looking at the spectra of all the metallic elements for the alloy Type 1 and Type 2 substrates, it can be seen that the spectral lines corresponding to the metallic states of these elements are slightly stronger for the Type 2 substrate, which means that the oxide layer for the Type 2 substrate is slightly thinner than for the Type 1 substrate.

Further differences are visible after a quantitative analysis of the spectra presented in Figure 9.

The atomic concentrations of metallic elements in the oxide layers were calculated taking into account intensities of the spectral lines corresponding only to oxidised states. The performed calculations showed that the concentration of titanium in the oxide layer on the Ti–13Nb–13Zr alloy Type 1 substrate was equal to 74 at. pct, the concentration of zirconium 13 at. pct and the concentration of niobium 13 at. pct. These concentrations are in accordance with the concentrations of these elements in the alloy. A quite different result was obtained for the alloy Type 2 substrate. The concentration of titanium was 57 at. pct, of zirconium 13 at. pct and of niobium 30 at. pct. This result shows that the chemical treatment resulted in the preferential oxidation of niobium over titanium.

One of the most important conditions for good coating adhesion is a good wetting of the substrate. The wettability properties of the substrate materials, pure titanium and alloy Type 1 and 2, are presented in Table III.

The contact angles of a water drop with a surface of the CP-Ti1 Type 1 and Type 2 substrates (85.8 ± 6.6 and 71.7 ± 16.1 deg, respectively) were higher than the alloy Type 1 and Type 2 substrates (71.0 ± 7.8 and 55.4 ± 3.5 deg, respectively). Differently, the diiodomethane contact angle of the CP-Ti1 Type 1 and Type 2 substrates (43.3 ± 5.2 and 37.9 ± 0.8 deg, respectively) were lower than the alloy Type 1 and Type 2 substrates (48.2 ± 4.4 and 54.7 ± 2.5 deg, respectively). The SFE of the alloy was higher than that of the CP Ti1 substrates. Besides this, the alloy Type 2 substrate to which the adhesion of the coatings was the highest had the highest SFE value and a larger share in the SFE value than the other investigated substrates. The polar component that measures the polarity of a surface is related to the bond strength between the substances.

It is known that the coating should have greater adhesion to the better wettable surface of the substrate. Thus, the wettability results correspond well with the adhesion of the sodium alginate coatings to the titanium biomaterials. Coating materials should penetrate the unevenness of the substrate and moisten a large surface, and the deposited coating should anchor mechanically in the substrate. Penetration of the polymer into pores of the oxide layer covering the surface of titanium biomaterials depends on the contact angle and the shape of the pores.

The CP-Ti1 Type 1 substrate was untreated (the as-received state in rolling conditions) and had the highest water wettability angle, which may be due to the presence of a thin rutile layer, deep scratches and rolling defects difficult to wet by liquid (Figure 10). On the contrary, the relatively flat surface of the alloy Type 2 (no open porosity in the surface was observed during SEM investigation) exhibited moderate wettability with a water contact angle of 55.4 ± 3.5 deg and the coating had very good adhesion to its surface. It is known from the literature that some materials (for instance adhesives) with an SFE lower than the substrate will easily wet the substrate and will form strong adhesive bonds. In our study, the SFE of the substrate materials was lower by 40 and 29 pct (in the case of the CP-Ti1 Type 1 and Type 2 substrates, respectively) as well as 34 and 23 pct lower (in the case of the alloy Type 1 and Type 2, respectively) than that of the coatings, which might contribute to the poor adhesion of the coatings. Nevertheless, this difference in the SFE values was the lowest for the alloy Type 2. In addition, this alloy...
exhibited moderate hydrophilicity, which indicates a relatively high contact area between the substrate and the drop of water. According to Kowalski *et al.*[46] a high contact area between the substrate and the coating may lead to physical interactions or bonds that form between the atoms of the two surfaces, resulting in surface wetting.

The adhesion mechanism of the coating to the substrate can be very complex and its evaluation is not straightforward.[42,47-49] In general, it can be related to (i) the mechanical interlocking of the coating in the case of very rough surfaces, (ii) the chemical bonding between the coating and substrate (interdiffusion adhesion), (iii) the interfacial adhesion when the adhesive forces are concentrated around a thin coating/substrate interface, or (iv) adhesion obtained by applying an intermediate layer or layers with different phase composition and properties between the substrate and the coating. Two of them, namely chemical bonding and mechanical interlocking adhesion, usually enable relatively high strength.[42,50] These mechanisms may exist separately or together. Therefore, a lot of attention

![Fig. 9—XPS spectra of Ti 2p (a), Zr 3d (b) and Nb 3d (c) lines for the Ti–13Nb–13Zr alloy Type 1 and Type 2 substrates.](image)
should be paid to the effect of surface preparation of the substrate before coating deposition. Unfortunately, this stage is often underestimated, and scientists focus on developing the coating itself and do not focus on the substrate.

Both the surface morphology and topography, as well as wettability, can affect the adhesion of the coating. On the one hand, the smooth surface of the substrate may make it difficult to achieve high coating adhesion due to the lower surface area and the inability to interlock mechanically with the substrate. On the other hand, if the coating is very rough, it may be difficult to wet and penetrate the surface unevenness of the coating. In this case, the resulting defects on the coating/substrate interface can lead to coating failure and delamination. Coating degradation can also be induced by wear or scratches, enabling the diffusion of surrounding media to the coating/substrate interface.[49] Adhesion of the coating can also be reduced by the high residual stresses in the coating/substrate system that occur as a result of the thermal and elastic mismatch between the coating and the underlying substrate or shrinkage while drying the coating. Thus, the understanding of the mechanisms responsible for coating adhesion is of great importance and may contribute to its enhancement.

Summarising the influence of substrates on the adhesion of coatings developed in this work, the investigation results of surface topography and morphology, surface chemistry and surface properties (wettability and SFE) indicate that chemical bonding can be plausible as the adhesion mechanism. Sodium alginate contains a number of free carboxyl and hydroxyl groups distributed along the backbone, which allows reactions with other atoms.[51] It is believed that the carboxylate groups are responsible for the bonding with the titanium biomaterial substrates, particularly with Ti and Nb atoms. The adsorption mechanism of sodium alginate molecules involving the bonding of carboxylate ligands to the metal atom (M) is shown in Figure 11. However, the interfacial adhesion mechanism could also participate.

Based on the XPS spectra, only one oxidation state of titanium Ti$^{4+}$ occurred in the CP-Ti1 Type 1 sample (adhesion class 0B), while three oxidation states, Ti$^{3+}$, Ti$^{2+}$ and Ti$, occurred in the CP-Ti1 Type 2 sample (adhesion class 2B). In the case of the alloy Type 1 sample, the Ti, Nb and Zr concentrations were close to the alloy chemical composition (adhesion class 0B was determined), while the preferential oxidation of Nb over Ti was present in the chemically-treated alloy Type 2 sample (the excellent adhesion class of 5B was determined). Due to the highest adhesion of the sodium alginate coating to this particular substrate.

Moreover, the coating exhibited the highest adhesion to the relatively flat alloy Type 2 substrate, free of pores and scratches. According to XPS investigation results, the oxide layer in both chemically-treated Type 2 substrates was also thinner than in the Type 1 substrates.

Due to the highest adhesion, the coatings on the CP-Ti1 Type 2 and the alloy Type 2 substrates were used for further investigation of microstructure, surface topography and wettability.

C. Microstructure and Surface Topography of the Coatings

The microscopically homogeneous coating deposited on the CP Ti1 Type 2 substrate from solution 8 at the voltage of 10 V and time of 300 s was submitted to detailed TEM and XRD investigations. The coating thickness measured in the TEM images taken from the cross-section of the sample was in the range of 840 to 980 nm (Figure 12). The coating was dense without the presence of pores and exhibited an amorphous structure (Figure 12, SAED pattern A). However, during the lamella preparation by FIB, detachment of the coating from the substrate covered by a passive oxide layer was observed, which is consistent with the relatively poor adhesion of this particular coating to the substrate (the adhesion class 2B was determined). It should also be mentioned that the FIB lamella preparation was a challenge in this specific case because sodium alginate as a polysaccharide polymer is sensitive by nature.[12] The oxide layer, 20 nm thick, was composed mainly of TiO$_2$ (rutile, tetragonal primitive) (Figure 12, SAED pattern B). TEM-EDS microanalysis of the chemical composition confirmed the presence of Na, O and C in the polymer, but some Ca was also detected.

GIXRD pattern of the coated CP Ti1 Type 2 is shown in Figure 13. The diffraction peak from SA was present at the 20 angle of around 14 deg. The strong diffraction peaks from the Ti x (hcp) phase confirmed very low coating thickness.

The surface topography images of the coatings on the CP-Ti 1 Type 2 and the alloy Type 2 substrates are shown in Figure 14, while the roughness parameters are shown in Table IV.

It was found that the investigated coatings were characterised by relatively low surface development. All the surface topography parameters of the coating on the CP-Ti1 exhibited higher values than the coating on the Ti–13Nb–13Zr substrate (Table IV). The $R_q$ and $R_a$ parameters for the coating on the CP-Ti1 Type 2 (0.73 ± 0.08 μm and 0.57 ± 0.07 μm, respectively) were more than twice as high as for the coating on the alloy Type 2 (0.32 ± 0.03 μm and 0.25 ± 0.03 μm, respectively). The $R_t$ parameter for the coating on the CP-Ti1 Type 2 (8.3 ± 2.3 μm) was about 40 pct higher than that of R$t$ (5.6 ± 3.4 μm) for the coating on the alloy Type 2. In comparison with the roughness of similar coatings electrophoretically deposited on the Ti–15Mo alloy described by Szklarska et al.,[15] the coating investigated in the present work had a higher roughness. These differences are probably due to the different roughness of the substrate used for EPD. Moreover, in this work, a ZnO interlayer was applied between the coatings and the Ti–15Mo alloy substrate.

It is worth mentioning that both coatings had an average of 10 to 15 pct higher surface topography parameters than the substrates on which they were
deposited. Such an observation allows the conclusion to be drawn that, regardless of the surface features (scratches or flat surface) and roughness of the substrate materials, the coatings have a more developed surface. There are also differences in the surface topography of both coatings. The one on titanium reflects the surface of the substrate and the irregularities follow the scratches (Figure 14(a)). The one on alloy is composed of irregularities distributed relatively evenly on its surface (Figure 14(b)).

D. Surface Properties

The wetting properties (e.g. contact angle, surface free energy) of coatings are very important in biomedical applications. They are closely connected with osseointegration and they have an impact on the occurring cellular process. Modification of the metallic surface (e.g. applying bioactive coatings) and proper wetting properties enables finer contact with natural tissue and increases the osseointegration or differentiation of cells and proliferation. \[52\]

The contact angle and surface free energy were measured for the coating deposited from solution 8 at the voltage of 10 V and time of 300 s on the CP-Ti1 Type 1 and Type 2 substrates, as well as on the alloy Type 1 and Type 2 substrates. The contact angle was measured for both solutions, pure water and diiodomethane, because they have different surface tension. Water has a polar character, while diiodomethane

| Material          | Diiodomethane Contact Angle [deg] | Water Contact Angle [deg] | SFE [mN/m] | Disperse component [mN/m] | Polar component [mN/m] |
|-------------------|-----------------------------------|---------------------------|------------|---------------------------|-----------------------|
| CP-Ti1 Type 1     | 43.3 ± 5.2                        | 85.8 ± 6.6                | 40.0 ± 4.5 | 37.9 ± 2.7                | 2.1 ± 1.8             |
| CP-Ti1 Type 2     | 37.9 ± 0.8                        | 71.7 ± 16.1               | 47.1 ± 7.3 | 40.7 ± 0.4                | 6.4 ± 6.9             |
| Alloy Type 1      | 48.2 ± 4.4                        | 71.0 ± 7.8                | 43.6 ± 6.2 | 35.3 ± 2.4                | 8.3 ± 3.8             |
| Alloy Type 2      | 54.7 ± 2.5                        | 55.4 ± 3.5                | 50.3 ± 3.7 | 31.6 ± 1.4                | 18.6 ± 2.3            |

Table III. The Wettability Properties of the CP-Ti1 Type 1 and Type 2 Substrates as Well as the Alloy Type 1 and Type 2 Substrates

Fig. 10—The scheme of the coating/substrate system showing good penetration of a liquid and therefore good adhesion to the substrate (a) and weak penetration of a liquid and therefore poor adhesion to the substrate (b).

Fig. 11—Adsorption of sodium alginate involving the bonding of carboxylate ligands to the metal atom (M). Reprinted with permission from Ref. \[53\].

Fig. 12—Microstructure of the SA coating on the CP-Ti1 Type 2 substrate deposited from solution 8 and SAED patterns taken from the areas indicated as A and B with identification (a) and the EDS spectrum taken from the area marked as A in (a) (b). TEM, FIB lamella.
(CH$_2$I$_2$) has a non-polar character. The average values of contact angle for both solutions and SFE for the coatings are presented in Table V. The contact angle for diiodomethane was higher for the coating on the alloy (49.9 ± 1.8 deg) than for the coating on pure titanium (37.4 ± 1.3 deg). Contrary to that, the water contact angle was higher for the coating on the titanium substrate (35.3 ± 3.1 deg) than for the coating on the alloy substrate (31.8 ± 1.9 deg). Nevertheless, the coating on both substrates exhibited moderate hydrophilicity and, in comparison with both substrates, the contact angles with water were much lower.

The SFE for SA coatings on the titanium (66.7 ± 2.3 mN/m) and the alloy (65.7 ± 2.2 mN/m) substrates was higher than the SFE for the substrates, 47.1 ± 7.3 mN/m and 50.3 ± 3.7 mN/m for the titanium and the alloy, respectively. In the case of the coating on the titanium substrate, the polar component responsible, among others, for the bond strength between materials had a smaller share in the SFE value than in the case of the coating deposited on the alloy substrate, in which both dispersive and polar components showed the same level. From the biological application point of view, a hydrophilic surface and high SFE are beneficial.$^{[52]}$

According to the literature,$^{[44]}$ the moderate wettability of polymers is preferable for effective cell adhesion.

IV. CONCLUSIONS

1. The homogeneity of the coatings depended significantly on the chemical composition of the solution as well as on the electrophoretic deposition parameters, voltage and time of deposition. Homogeneous coatings were obtained from a colloidal solution consisting of 4 g/L SA and a dispersion phase containing a distilled water to ethanol volume ratio of 60/40 at a voltage of 10 V and a deposition time of 5 minutes. The coatings deposited from the solution with a lower SA concentration (2 g/L) were very thin and contained large bubbles. A higher SA concentration (8 g/L) in the solution led to coatings being obtained with SA precipitates and bubbles.

2. The adhesion of sodium alginate coatings depended significantly on the type of substrate, CP Ti1 or Ti–13Nb–13Zr alloy, and the substrate surface preparation route before the EPD process. Among the set of differently prepared substrates, the coatings had high adhesion (class 4B) to the polished and subsequently chemically-treated alloy (Type 2) only. Based on morphology and surface topography, surface chemistry and properties, wettability and SFE investigation results, chemical bonding was indicated as the main mechanism responsible for the coating adhesion. It was found that the preferential oxidation of Nb over Ti takes place in the chemically-treated alloy Type 2 substrate. Additionally, the interfacial adhesion mechanism could also be involved due to the lowest water contact angle and the highest SFE on this specific substrate compared with other substrates.

3. The coatings were dense and homogeneous without the presence of pores and exhibited an amorphous structure. The thickness of the coatings varied in the...
Table IV. The Roughness Parameters of the Coating Deposited From Solution 8 at the Voltage of 10 V and Time of 5 min on the CP-Ti1 Type 2 and Alloy Type 2 Substrates

| Material                  | $R_a$ [μm] | $R_s$ [μm] | $R_t$ [μm] |
|---------------------------|------------|------------|------------|
| SA Coating on the CP-Ti1 Type 2 | 0.73 ± 0.08 | 0.57 ± 0.07 | 8.3 ± 2.3  |
| SA Coating on the Alloy Type 2 | 0.32 ± 0.03 | 0.25 ± 0.03 | 5.6 ± 3.4  |

The parameters were obtained from optical profilometry measurements.

Table V. The Wettability Properties of the SA Coating Deposited From Solution 8 at the Voltage of 10 V and Time of 5 min on the CP-Ti1 Type 2 and the Alloy Type 2 Substrates

| Coating          | Diodomethane Contact Angle [deg] | Water Contact Angle [deg] | SFE [mN/m] | Disperse Component [mN/m] | Polar Component [mN/m] |
|------------------|----------------------------------|---------------------------|------------|--------------------------|------------------------|
| On the CP-Ti1 Type 2 | 37.4 ± 1.3                       | 35.3 ± 3.1                 | 66.7 ± 2.3 | 40.9 ± 0.6                | 25.8 ± 1.6             |
| On the Alloy Type 2    | 49.9 ± 1.8                       | 31.8 ± 1.9                 | 65.7 ± 2.2 | 34.4 ± 1.0                | 31.3 ± 1.2             |

range of 840 to 980 nm. The coatings exhibited relatively low surface development. The surface development was higher in the coatings deposited on the CP-Ti1 Type 2 than on the Ti–13Nb–13Zr alloy Type 2 substrates due to the higher roughness of the CP-Ti1 Type 2 substrate.

4. The coatings on both the CP-Ti1 and alloy substrates exhibited a hydrophilic nature. The water contact angle for the coatings was lower than the water contact angle for the substrates, whereas the surface free energy of the coatings was, on average, 30 pct higher than that of the substrates.

This work provides an insight into knowledge on the electrophoretic deposition of sodium alginate on titanium biomaterials and especially on the effect of substrate type and preparation route on coating adhesion. In the future, the obtained knowledge could be useful for the development of composite sodium alginate-based coatings on titanium alloys for biomedical applications.

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CONFLICT OF INTEREST

On behalf of all authors, the corresponding author states that there is no conflict of interest.

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