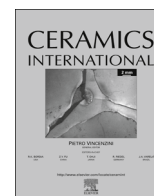




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Electrophoretic deposition of chitosan/Bioglass[®] and chitosan/Bioglass[®]/TiO₂ composite coatings for bioimplants

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ABSTRACT

Electrophoretic deposition (EPD) method has been developed for the fabrication of chitosan/Bioglass[®] and chitosan/Bioglass[®]/TiO₂ composite coatings on stainless steel substrates for biomedical applications. Microstructure, thickness, and mechanical properties, such as Vickers microhardness, compressive strength, and elastic modulus were determined. The use of chitosan enabled the co-EPD of Bioglass[®] and TiO₂ particles and offered the advantage of room temperature processing typical of EPD. The coating composition was varied by the combination of Bioglass[®] and TiO₂ concentrations in the chitosan solutions used for EPD. The cathodic deposition yield was studied at constant voltage for various deposition times. The coatings were microstructurally characterized by scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS). Homogeneous chitosan/Bioglass[®] coatings on stainless steel substrates were obtained at constant voltage condition using aqueous suspensions based on 0.016 wt% chitosan and 2 wt% Bioglass[®]. The addition of TiO₂ nanopowder to the composite coating was confirmed to improve the hardness, Young's modulus and compressive strength of the base chitosan/Bioglass[®] coating.

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1. Introduction

Composite materials are currently under investigation for applications in biomedical implants. The use of polymers to prepare biomedical coatings suggests the advantage of low temperature processing and flexibility of coatings. Important attention is being paying to the formation of composite coatings containing different bioceramics in a chitosan matrix.

Bio-based polymer films are principally prepared from polysaccharides, proteins and/or lipids, and they are generally biodegradable, non-toxic and edible materials. Chitin is the second most everywhere natural polysaccharide on the Earth after cellulose and it is composed of β (1→4)-linked 2-acetamido-2-deoxy- β -D-glucose (N-acetylglucosamine) [1]. It is structurally identical to cellulose, but it has acetamide groups (–NHCOCH₃) at the C-2 positions. The main derivative of chitin is chitosan, a linear polymer of α (1→4)-linked 2-amino-2-deoxy- β -D-glucopyranose which is easily derived by alkaline N-deacetylation. To a varying

extent characterized by the degree of deacetylation, chitosan is thus a copolymer of N-acetylglucosamine and glucosamine [2].

Chitosan is one of the most promising natural biopolymers for biomedical applications including tissue engineering and biomedical coatings [2–7] and it has attracted considerable interest in the biomedical field because of its excellent biodegradability, biocompatibility, antimicrobial activity and ability to accelerate wound healing properties [2–6].

To achieve a coating with homogeneous mechanical properties, a composite structure is desirable and special attention has been given to the development of organic–inorganic composites by dispersing ceramic particles within a polymer matrix [7]. Chitosan coatings have been obtained by cathodic electrophoretic deposition in previous research [8,9]. Bioactive glasses have excellent bioactivity and biocompatibility, they are used in several biomedical applications, for example non-load-bearing implants, bone cements, tissue engineering scaffolds, drug delivery systems, and bioactive coatings [10–14]. In particular, composite materials incorporating bioactive glasses are being considered promising for applications in biomedical coatings [7,15–17]. Different processes are possible for the deposition of a bioactive glass layer on metallic substrates such as plasma spraying, chemical vapor deposition, dip coating, electrophoretic deposition (EPD) and electrochemical

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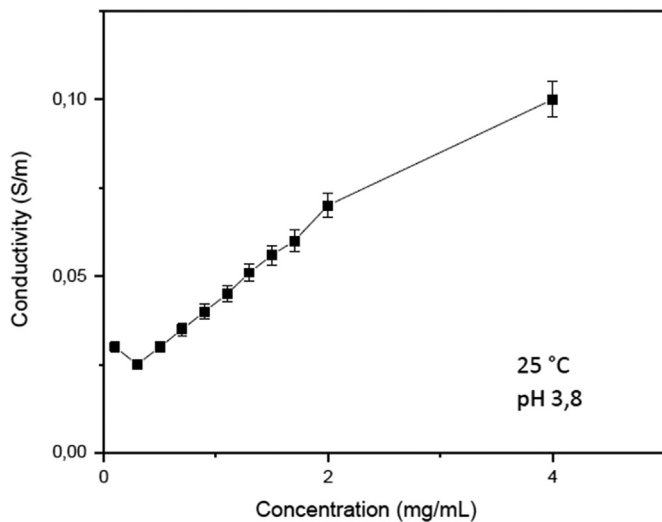


Fig. 1. The electrolytic conductivity behavior of chitosan dissolved in 0.1 M acetic acid solution at different concentrations.

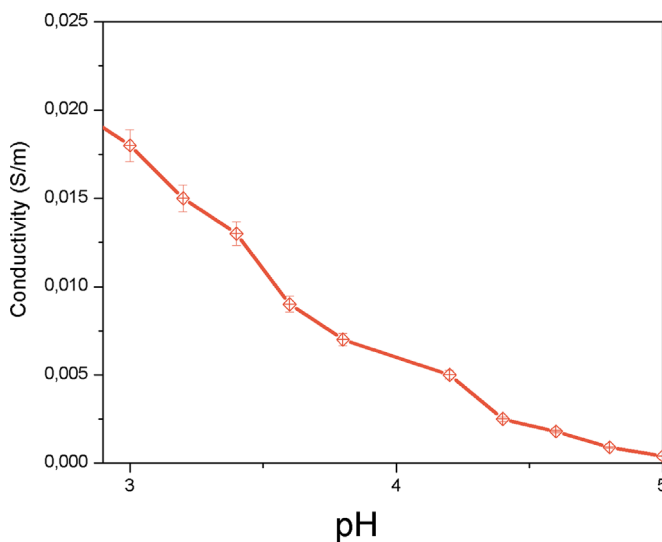


Fig. 2. Conductivity of chitosan dilute solutions as a function of pH at concentration of 0.016 wt%, and temperature of 25 °C.

deposition. The coating process not only influences the production cost, but will also affect the coating structure, the adhesion strength to the substrate, the porosity (shape, size morphology), and in this way the coating bioactivity.

The method applied in this study in order to coat metallic substrates with Bioglass[®] particles combined with a chitosan matrix is EPD, which is an electrochemical method highly considered for production of composite coatings [7]. The attraction of EPD lies in its simplicity; EPD is a cost-effective method usually requiring limited equipment and it offers the possibility of forming

coatings on substrates of complex shapes. In addition, EPD has the advantage to employ very short processing time, and it can be extended to commercial applications [18–21]. Previous studies have investigated the EPD of chitosan/Bioglass[®] films [7,22], however there has not been a detailed study about the mechanical properties of this type of coatings.

The goal of this research was the manufacture of a new family of composite coating based on chitosan, incorporating Bioglass[®] and TiO₂ nanoparticles in a chitosan matrix by co-EPD and analyzing the influence of TiO₂ nanoparticles on the mechanical properties of chitosan/Bioglass[®] coatings. Physical and mechanical properties (thickness, compressive strength, hardness and Young's modulus) were determined and the results were used to explain the observed combined effects of addition of bioactive glass and TiO₂ nanoparticles in the chitosan matrix.

2. Material and methods

2.1. Starting materials

Medium molecular weight chitosan (MW = 80 kDa; acetylation ~85%, Sigma-Aldrich) and 45S5 Bioglass[®] powder with nominal composition: 45 SiO₂–24.5 Na₂O–24.5 CaO–6 P₂O₅ (wt%) with typical particle size of 6 μm were used. Titanium dioxide nanoparticles (TiO₂-P25, Degussa, Evonik Industries) containing 80% anatase and 20% rutile with surface area of about 50 m² g⁻¹ and primary particle size of 21 nm were used. Distilled water, hydrochloric acid and NaOH (Tetrahedron lab, both) were used to prepare solutions in different concentrations in order to fix the pH.

Scanning electron microscopy (SEM) equipped with EDS analysis (SEM Philips 515) was used to characterize the microstructure of samples and to determine the coatings thickness by direct measurement on cross-sections images.

2.2. EPD of chitosan/45S5 Bioglass[®] and chitosan-Bioglass[®]-TiO₂ composite coatings

Bioglass[®] powder suspensions (2 wt% solids) were prepared using distilled water as a solvent to which 0.016 vol% of chitosan was added for each 100 ml of distilled water. The pH of the suspensions was adjusted using hydrochloric acid and NaOH solution (both, 0.1 M). TiO₂ nanopowder with a concentration of 0.5–1.5 wt% was added to chitosan suspensions. Glass jars containing the suspensions were placed into an ultrasonic bath for 30 min in order to disperse the particles and to dissolve agglomerates. Moreover, before each EPD experiment, the suspension was stirred magnetically for 45 min to maintain the stability of the suspension. The EPD process was carried out using stainless steel (AISI 316 L) foils (0.2 mm of thickness) as substrates, employing a PASCO power supply SE-9721A (PASCO Instrument, Roseville, USA). Since EPD of chitosan is strongly influenced by the pH, the pH of the suspensions was measured by pH Meter (Hanna's HI 3220). The dependence of deposited weight as function of time was estimated by comparing the electrode weight before and after deposition. The dependence of chitosan/Bioglass[®]/TiO₂ (Ch-BG-T) suspension

Table 1

Composition of suspensions used for EPD of chitosan/Bioglass[®] coatings.

Suspension	pH	Chitosan concentration per ml of distilled water [g/ml]	Bioglass [®] concentration per ml of distilled water [g/ml]	Current density mA/cm ²
N° 1	3	0.0016	0.010	0.501
N° 2	3.2	0.0016	0.015	0.485
N° 3	3.8	0.0016	0.018	0.609
N° 4	4	0.0016	0.020	0.435

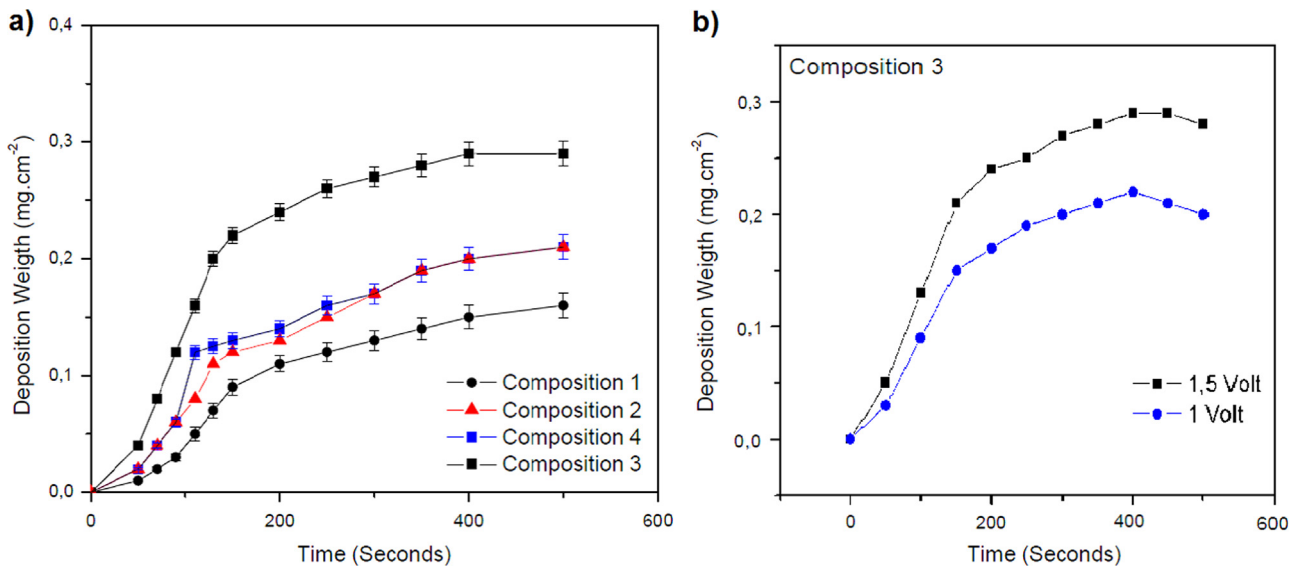


Fig. 3. Effect of the composition of the suspension in the deposition of chitosan-Bioglass® coatings (composition of the suspensions in Table 1).

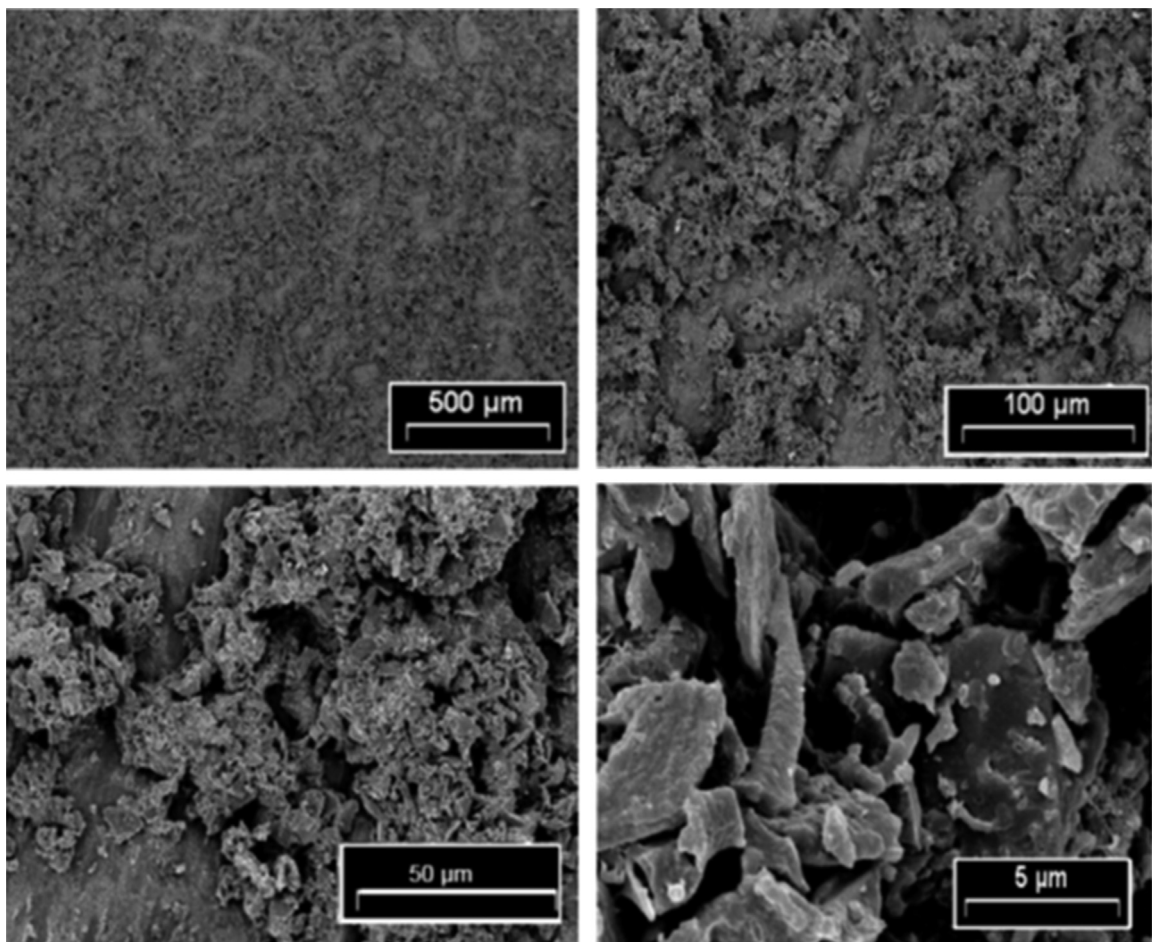


Fig. 4. SEM micrograph of green chitosan/45S5 Bioglass® composite coating on stainless steel (top view) at different magnifications. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

conductivity on pH values was determined using a Delta CO044 conductivity meter. EPD was performed at constant voltage in the range 0.5–2.5 V at 23 ± 2 °C for different time periods in the range 0–600 s. The coatings were dried for 24 h and then the weight gain per substrate area was determined by a precision balance with 0.01 mg resolution (Kern ABT 100-5M).

2.3. Mechanical properties

Mechanical properties of coatings were investigated. A texture analyser TA-XT2i (Stable Microsystems, United Kingdom) was used in order to measure the mechanical properties based on the ASTM standard D882. For these mechanical tests at least ten samples

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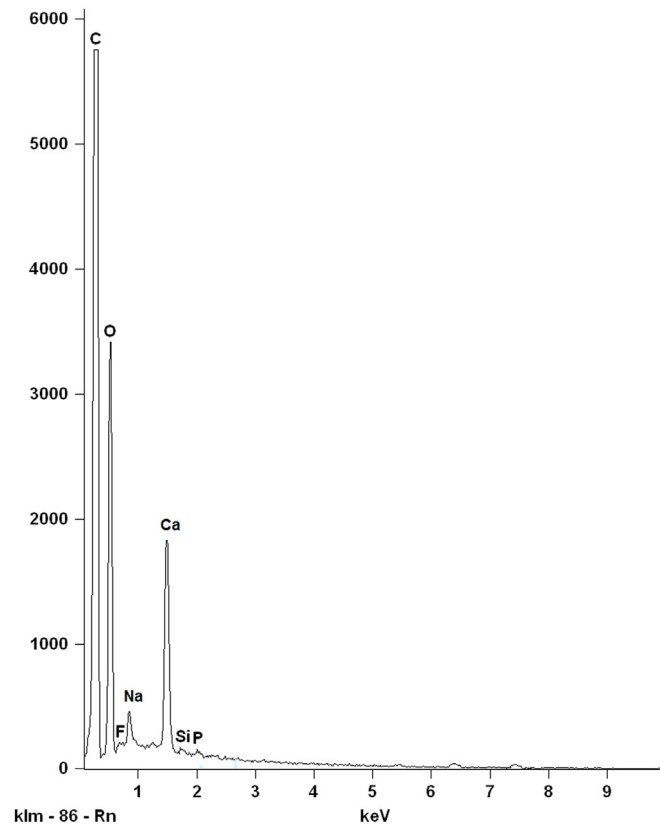


Fig. 5. EDS microanalysis of sample represented by Fig. 4(a–d).

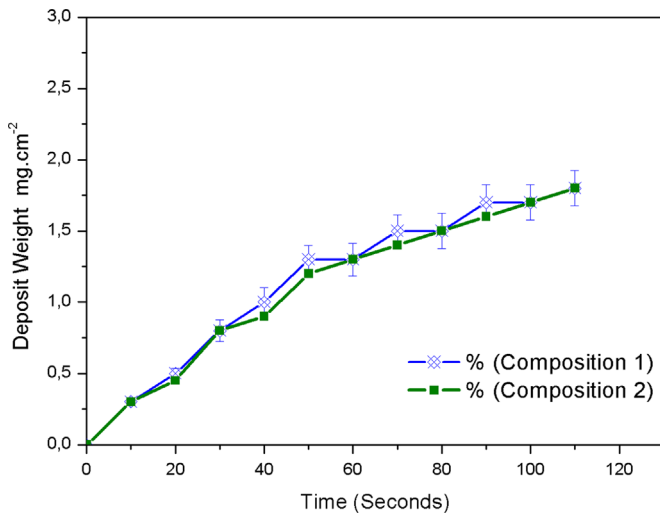


Fig. 6. Deposition weight vs. time of chitosán-Bioglass[®]-TiO₂ coatings for different compositions. The experiments have been carried out applying 1.5 V.

were used per each mentioned type, and the results were averaged. The Young's modulus (E) was evaluated as the slope of the initial linear portion of stress–strain curves [23]. The hardness of the tested samples was measured using a Vickers microhardness tester (FV-300, Future Tech, PRC), under a load of 100 g for 10 s, the average hardness values were obtained from 10 determinations (indents) per sample.

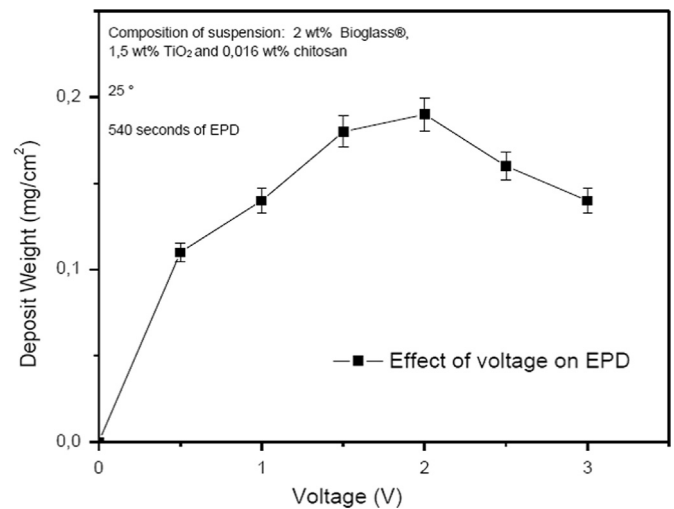


Fig. 7. Effect of the voltage on EPD deposit weight of chitosan/Bioglass[®]/TiO₂ composite coating.

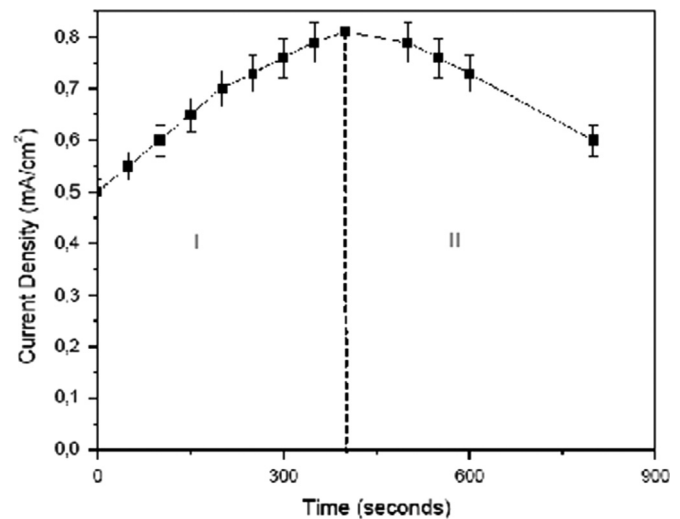


Fig. 8. Effect to current density vs. EPD time.

3. Results and discussion

3.1. EPD process

3.1.1. EPD of chitosan/Bioglass[®] (Ch-BG) composite coatings

Since chitosan is a charged polycation, it was anticipated that cathodic electrophoretic process would lead to preparation of chitosan coatings. Chitosan does not dissolve adequately in pure water and precipitates at high values of pH. A water–acetic acid solution was used to solve chitosan fixing the pH of suspensions at values between 3.5 and 4.

EPD was performed from chitosan solutions containing Bioglass[®] in different concentrations. The electrolytic conductivity behavior of chitosan in acid solution was studied. The specific conductivity of distilled water was 0.5 $\mu\text{S}/\text{cm}$. All measurements were performed at temperature of 25 °C.

In a 0.1 M acetic acid solution, there are dissociated carboxylic acidic ions ($\text{R}-\text{COO}^-$), proton (H^+) and undissociated carboxylic acid molecules ($\text{r}-\text{COOH}$). When chitosan dissolves in these weak acid solutions, amino groups first bind dissociated H^+ leading to the slight decrease of specific conductivity, at this time, free ions and chitosan chains carrying positive charges repel each other because of electrostatic repulsion. When the dissociated H^+ are

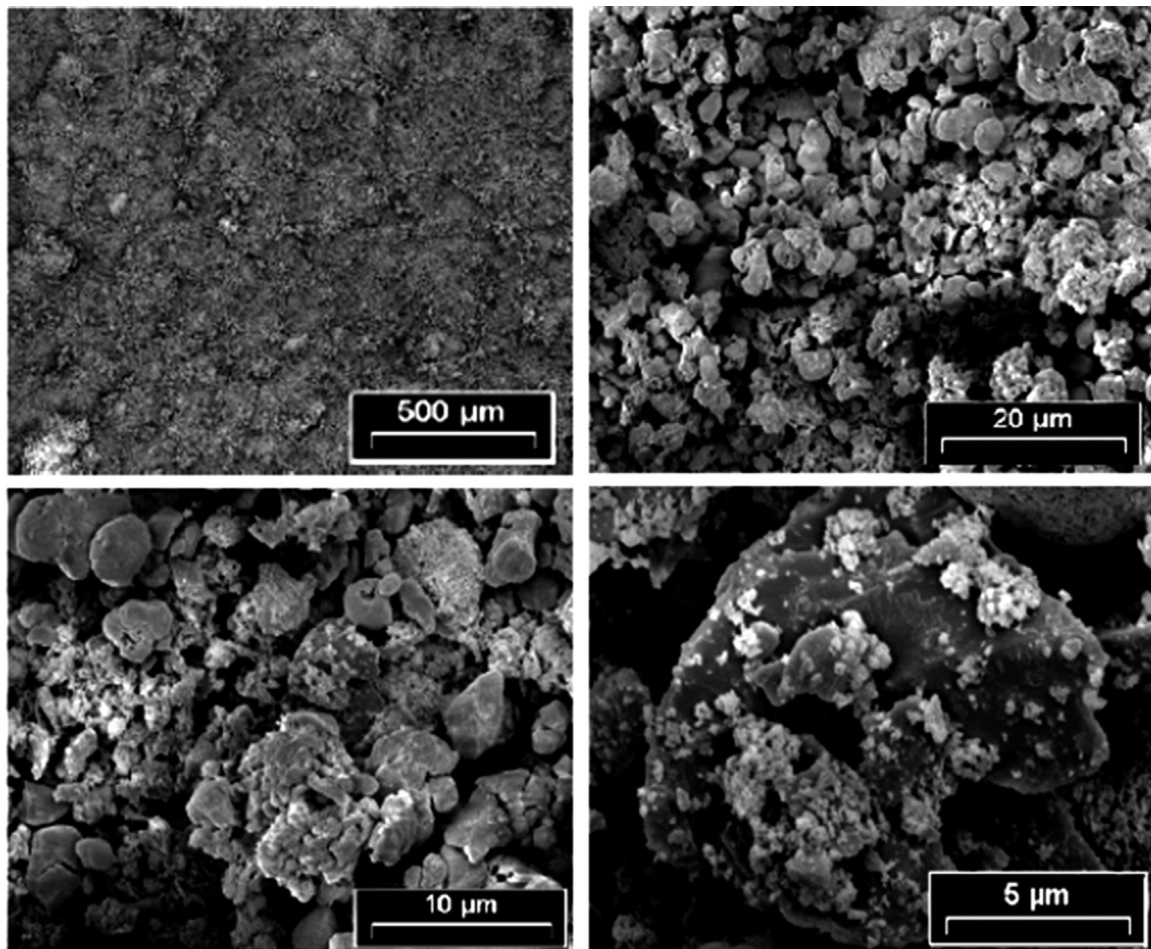
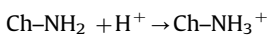


Fig. 9. Surface morphologies of chitosan/Bioglass[®]/TiO₂ coatings applying 2 V during 2 min.

bound completely to chitosan, with increasing chitosan concentration, more chitosan molecules begin to interact with undissociated carboxylic acid molecules which transport the charge, so, the specific conductivity of the chitosan solution increases too. Fig. 1 shows the electrolytic conductivity behavior of chitosan in different solutions of varying concentrations confirming this behavior.

By trial-and-error it was determined that for use in EPD, chitosan concentrations below 2 mg/ml of solvent were required to promote the migration of the molecules to the cathode. Fig. 2 displays the dependence of chitosan solution conductivity on pH, showing that the conductivity of the chitosan solution decreases with increasing pH. At low pH, free amino groups of chitosan are protonated and it becomes a cationic polyelectrolyte:



EPD suspensions were prepared containing 1 and 2 wt% of Bioglass[®] in distilled water at pH 3.8. Next, 0.016 wt% of chitosan was added. The compositions of the prepared suspensions are shown in Table 1. Cathodic EPD of Ch-BG composite has been performed in previous studies. Pishbin et al. [7], for example, reported that uniform Bioglass[®] deposition can be achieved at relatively low Bioglass[®] concentrations, which avoids a massive deposition of bioactive glass particles on the cathode.

Fig. 3(a) shows the effects of deposition rate as function of time for different compositions of chitosan/Bioglass[®] suspensions using 1.5 V. Fig. 3(b) shows the time-dependent variation of deposited weight at different applied voltages. After a trial-and-error approach, the optimal condition for the EPD process was achieved

using a constant voltage of 1.5 V during 2 min at pH=3.2 when a suspension with 0.016 wt% of chitosan was used. The results show that initially the deposited weight increases with deposition time (50 s) and then, the deposited weight deviates from linearity indicating a decrease of deposition rate as the coating thickness increases.

The EPD of chitosan from aqueous solution is accompanied by production of hydrogen gas on the cathode. However, when the voltage is relatively low, a dense deposit of Ch-BG is formed (Fig. 4). Microanalysis results by EDS of coatings shown in Fig. 4 are reported in Fig. 5. Peaks corresponding to carbon, silicon, sodium, oxygen, calcium and phosphorus were identified (C: 68%; Si: 2%; O: 19%; Ca: 9%). The EDS spectrum of the sample is consistent with the elements present in the Ch-BG composite coating.

3.1.2. EPD of chitosan/Bioglass[®]/TiO₂ (Ch-BG-T) composite coatings

Bioglass[®] suspensions with 2 wt% of solid were prepared using distilled water as a solvent and 0.016 wt% of chitosan was added for each 100 ml of Bioglass[®] suspension. Different amounts of TiO₂ nanopowder (0.5–1.5 wt%) were added to Ch-BG suspensions. Cathodic deposits were obtained applying a voltage between 0.5 and 2.5 V. The deposition time was evaluated in the range of 2–5 min. The formation of chitosan/Bioglass[®]/TiO₂ coatings indicated that Bioglass[®] particles and TiO₂ nanoparticles were adsorbed to positively charged chitosan chains. Fig. 6 shows deposition weight vs deposition time for the Ch-BG-T composite coating with a composition of 2 wt% Bioglass[®], 0.5 wt% TiO₂ and 0.016 wt% chitosan (curve 2) and composition of 2 wt% Bioglass[®], 1.5 wt% TiO₂ and 0.016 wt% chitosan (curve 1). It can be observed that the

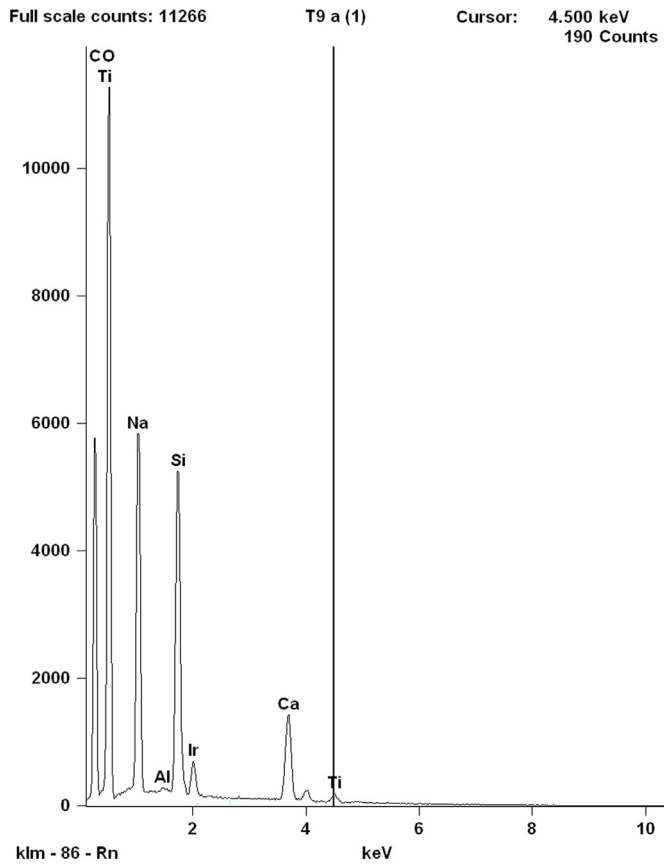


Fig. 10. EDS microanalysis of chitosan/Bioglass[®]/TiO₂ composite coating.

Table 2
Thickness of EPD films prepared under different conditions.

Type of film	Time of EPD (seconds)	Thickness (μm)	
		Before TiO ₂ addition	After TiO ₂ addition (2 wt%)
Chitosan/Bioglass [®] films deposited applying 2 V for 2–4 min from suspension containing 2 wt% Bioglass [®] and 0.016 wt% chitosan	120	10.5 ± 0.2	10.8 ± 0.1
	240	14.5 ± 0.2	15.4 ± 0.2
	360	16.3 ± 0.2	16.9 ± 0.2
Chitosan/Bioglass [®] films deposited applying 1.5 V for 2–4 min from suspension containing 2 wt% Bioglass [®] and 0.016 wt% chitosan.	120	5.7 ± 0.1	6 ± 0.1
	240	7.2 ± 0.2	7.5 ± 0.1
	360	9.2 ± 0.3	9.5 ± 0.2

deposition weight increased with increasing deposition time, consequently forming deposits of different thicknesses (Table 2).

Fig. 7 shows the dependence of the weight of chitosan/Bioglass[®]/TiO₂ composite coating on voltage. In this graph it is possible to observe that the optimal voltage for EPD of chitosan/Bioglass[®]/TiO₂ composite coatings is in the range of 1–2 V. Fig. 8 shows the variation of the current density with deposition time when 2 V was applied. The current is important for determination of the deposition rate in region (I). The current increases in relation to the increase of deposition rate in this period. However, the increase of current density becomes less pronounced and deposition rate is mainly determined by the current density in the region II. So, there is only a moderate decrease in deposition rate compared with region I. A similar behavior is observed up to 2.5 V. Then, for higher voltages, water electrolysis starts and

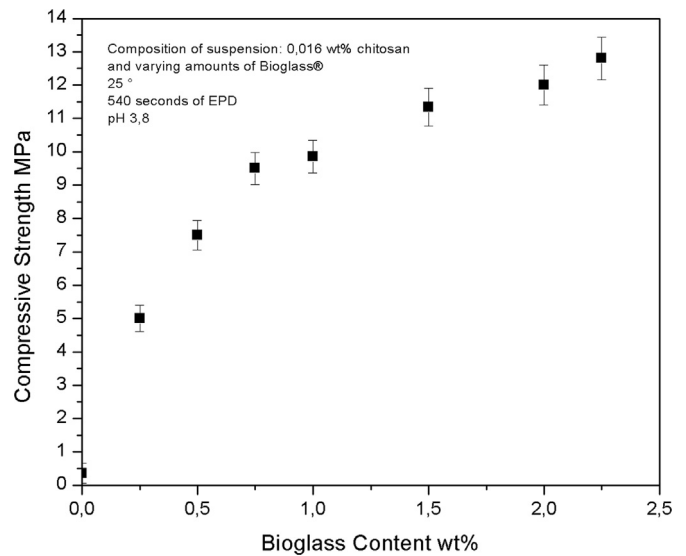


Fig. 11. Compressive strength of chitosan/Bioglass[®] coating vs. Bioglass[®] amount.

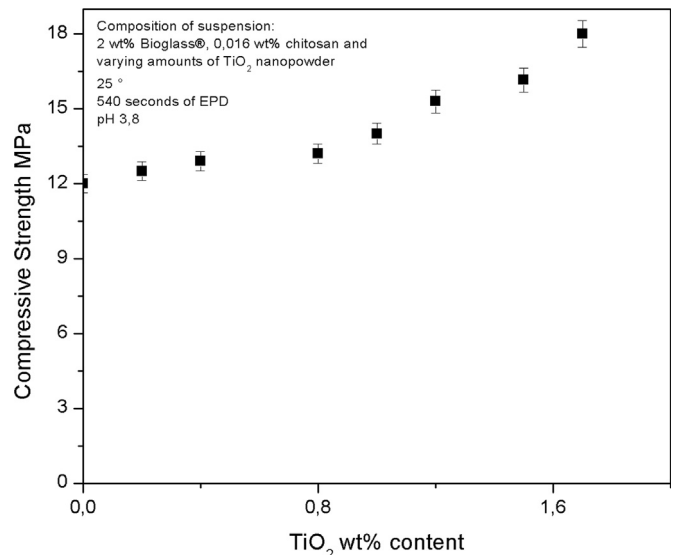


Fig. 12. Compressive strength of chitosan-Bioglass[®]-TiO₂ composite as a function of TiO₂ amount.

Table 3
Young's modulus (E) and compressive strength (CS) corresponding to chitosan-Bioglass[®] and chitosan-Bioglass[®]-TiO₂ films, deposited applying 2 V for 2 min.

Chitosan/Bioglass [®] film			Chitosan/Bioglass [®] /TiO ₂ film		
CS (MPa)	E (MPa)	Thickness (μm)	CS (MPa)	E (MPa)	Thickness (μm)
12.3 ± 0.1	40.6 ± 1.8	10.5 ± 0.2	14.6 ± 3.8	62.6 ± 4	10.8 ± 0.1

Table 4
One-way ANOVA for Young's modulus measurement on coatings.

One-way ANOVA for Young's modulus				
Source	D.F	Sum of squares	Mean squares	F ratio
Presence of TiO ₂	1	27,611	27,611	12,225
Error	16	3614	226	
Total	17	31,225		

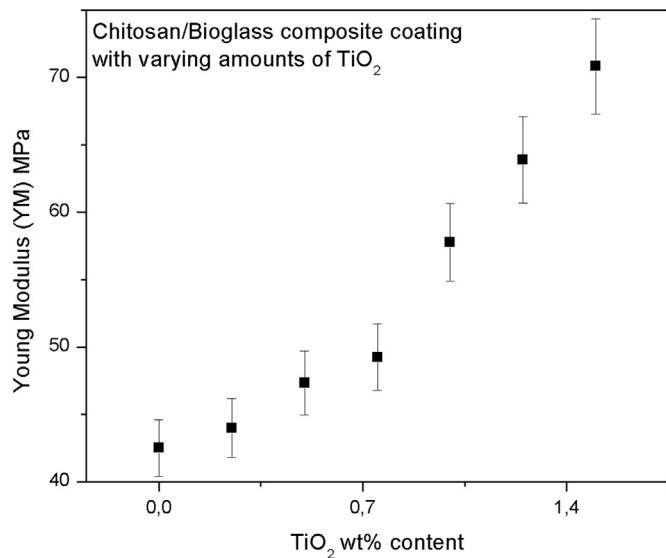


Fig. 13. Young's modulus of chitosan-Bioglass[®]-TiO₂ composite coatings vs a TiO₂ content

Table 5

Rupture stress of chitosan/Bioglass[®] and chitosan/Bioglass[®]/TiO₂ composite films.

Rupture stress (RS) %	
Chitosan/Bioglass [®]	Chitosan/Bioglass [®] /TiO ₂
31.5 ± 0.9	20.4 ± 3.9
33.2 ± 1.2	19.3 ± 0.7
29.4 ± 2.5	18.5 ± 1.2
30.9 ± 3.5	17.3 ± 1.6
28.1 ± 3.8	21 ± 0.6
35.7 ± 1	20.9 ± 1
26.3 ± 4.6	22.7 ± 2.3
29.5 ± 1.2	20.5 ± 2
26.5 ± 3.6	22.4 ± 4.6

consequently coatings with reduced adherence to the substrate and relatively low homogeneity are obtained.

In Fig. 9 the microstructure (top view) of chitosan/Bioglass[®]/TiO₂ coatings deposited at 2 V, 2 min can be observed, these were considered as optimal EPD conditions for the Ch-BG-T system as they led to homogeneous, well adhered coatings. Observation at low magnifications (Fig. 9(a) and (b)) indicates that the bioactive glass particles and TiO₂ nanoparticles are embedded in the chitosan matrix with non-uniform distribution. It is possible to observe some agglomerations of Bioglass[®]. At higher magnification (Fig. 9(d)) more details of the surface morphology and the presence of agglomerates adhered to Bioglass[®] microparticles, probably titania nanoparticles, are observed. The observation of SEM micrographs indicates that the coatings are crack-free. It was also found that it was not possible to obtain coatings for this composite system at voltages lower than 1 V. EDS microanalysis (Fig. 10) shows peaks matched to carbon, silicon, sodium, oxygen, titanium, calcium and phosphorus, as expected. These coatings exhibited greater homogeneity than coatings without titania when they were observed macroscopically.

3.2. Structural and mechanical properties

3.2.1. Mechanical properties

Fig. 11 shows the effect of different Bioglass[®] concentrations on the compressive strength of chitosan-Bioglass[®] composite

coatings. The Ch-BG-T coatings were fabricated by EPD applying 2 V during 2 min. The increase of the concentration of Bioglass[®] particles in the EPD suspension resulted in a rather linear increase in compressive strength. The pure chitosan coating on stainless steel exhibited a compressive strength of 0.38 MPa, when Bioglass[®] powder was added, a higher compressive strength, up to nearly 13 MPa, was measured. However, when the Bioglass[®] content exceeded 1.5%, the compressive strength exhibited constant values and the coatings showed brittle behavior produced by the relatively high proportion of inorganic phase. Similar response was obtained with addition of TiO₂ nanoparticles to the chitosan-Bioglass[®] composite from suspensions with 2 wt% Bioglass[®]/0.016 wt% chitosan, as shown in Fig. 12. The addition of 2 wt% TiO₂ to Ch-BG coating led to an increase of compressive strength up to 18 MPa. The Young's modulus is essential for the adequate design of coatings that must have a certain degree of stiffness to enable effective contact with bone tissue. The measured values of the Young's modulus (E) are given in Table 3.

One-way ANOVA on Young's modulus values was performed for two types of samples according to the presence or absence of TiO₂ nanoparticles in chitosan/Bioglass[®] coatings. The results are shown in Table 4. The F score is well below the 0.05 threshold, so that the groups are statistically significantly different from one another. Fig. 13 summarizes the effect of TiO₂ nanoparticles on Young's modulus of Ch-BG composite coatings. By the addition of TiO₂, the Young's modulus and compressive strength of Ch-BG composites were both enhanced compared with the coating without TiO₂. The increase in mechanical properties of Ch-BG-T composite coatings is related to the introduction of rigid titania particles, which act as a secondary inorganic reinforcement phase when the correct proportion of inorganic and organic phases is present in the composite coatings.

The Vickers micro-hardness of the chitosan-Bioglass[®] composite coating was 80 ± 4 MPa whilst it was 95 ± 6 MPa for the chitosan/Bioglass[®]/TiO₂ composite coating. These values are expected due the higher content of inorganic phase in the coatings. The effect of TiO₂ amount on the elongation at break is shown in Table 5. The results show that the incorporation of TiO₂ nanoparticles leads to a decrease in material ductility. The mechanical properties can be linked to the physico-chemical characteristics of the films, in particular to the content of inorganic phase (Bioglass[®] and TiO₂). In this study the compressive strength, hardness and modulus increased ($P < 0.05$) and the elongation at break decreased when the TiO₂ content increased. Thus addition of TiO₂ nanoparticles can be conveniently used to tune the coating mechanical properties without modifying the Bioglass[®] content.

4. Conclusions

Homogeneous chitosan/Bioglass[®] composite coatings on 316 L stainless steel substrates were fabricated by EPD from aqueous suspensions applying 1.5 V during 2 min. The results obtained in this study indicate the possibility to add TiO₂ nanoparticles by a single EPD process to the chitosan-Bioglass[®] coatings in order to improve the mechanical properties of the coatings. The most suitable EPD conditions for Ch-BG-T composite coatings in terms of coating homogeneity were 2 V and 2 min when using aqueous suspensions based on 0.016 wt% chitosan, 2 wt% Bioglass[®], 2 wt% TiO₂.

Significant improvement in the Young's modulus and compressive strength was obtained by incorporating TiO₂ nanoparticles in Ch-BG coatings. The results of this study indicate that TiO₂ plays an important role in the enhancement of the mechanical properties of Ch-BG composite coating, thus addition of TiO₂ nanoparticles can be employed to tune the mechanical properties

of the coatings without modifying the Bioglass[®] particle content. The microstructure and morphology of Ch-BG-T coatings were reproducible and EPD can thus be considered a convenient low cost method to produce chitosan/Bioglass[®]/TiO₂ composite coatings of variable mechanical properties for biomedical applications.

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References

- [1] C. Pillai, P. Willi, C. Sharma, Chitin and chitosan polymers: chemistry, solubility and fiber formation, *Prog. Polym. Sci.* 34 (2009) 641–678.
- [2] M. Rinaudo, Chitin and chitosan: properties and applications, *Prog. Polym. Sci.* 31 (2006) 603–632.
- [3] H. Harmoudi, L. Gaini, E. Daoudi, M. Rhazi, Y. Boughalebc, M. Mhammedi, A. Migalska-Zalas, M. Bakassea, Removal of 2,4-D from aqueous solutions by adsorption processes using two biopolymers: chitin and chitosan and their optical properties, *Opt. Mater.* 36 (2014) 1471–1477.
- [4] O. Lopez, M.A. Garcia, M.A. Villar, A. Gentili, M.S. Rodriguez, L. Albertengo, Thermo-compression of biodegradable thermoplastic corn starch films containing chitin and chitosan, *Food Sci. Technol. Res.* 57 (2014) 106–115.
- [5] R. Jayakumar, M. Prabaharan, P.T. Sudheesh Kumar, S.V. Nair, H. Tamura, Biomaterials based on chitin and chitosan in wound dressing applications, *Bio-technol. Adv.* 29 (2011) 322–337.
- [6] Q. Yao, P. Nooeaid, J. Roether, Y. Dong, Q. Zhang, A. Boccaccini, Bioglass[®]-based scaffolds incorporating polycaprolactone and chitosan coatings for controlled vancomycin delivery, *Ceram. Int.* 39 (2013) 7517–7522.
- [7] F. Pishbin, A. Simji, M.P. Ryan, A.R. Boccaccini, Electrophoretic deposition of chitosan/45S5 Bioglass[®] composite coatings for orthopaedic applications, *Surf. Coat. Technol.* 205 (2011) 5260–5268.
- [8] A. Simchi, F. Pishbin, A.R. Boccaccini, Electrophoretic deposition of chitosan, *Mater. Lett.* 63 (2009) 2253–2256.
- [9] F. Gebhardt, S. Seuss, M.C. Turhan, H. Hornberger, S. Virtanen, A.R. Boccaccini, Characterization of electrophoretic chitosan coatings on stainless steel, *Mater. Lett.* 66 (1) (2012) 302–304.
- [10] M. Monsalve, H. Ageorges, E. Lopez, F. Vargas, F. Bolivar, Bioactivity and mechanical properties of plasma-sprayed coatings of bioglass powders, *Surf. Coat. Technol.* 220 (2013) 60–66.
- [11] C. Berbecarua, G.E. Stanb, S. Pinac, D.U. Tulyaganovc, J.M.F. Ferreira, The bioactivity mechanism of magnetron sputtered bioglass thin films, *Appl. Surf. Sci.* 258 (2012) 9840–9848.
- [12] X. Renlong, Q. Zhang, G. Jiacheng, Identification of the wollastonite phase in sintered 45S5 bioglass and its effect on in vitro bioactivity, *J. Non-Cryst. Solids* 356 (2010) 1180–1184.
- [13] M. Fathi, A. Doostmohammadi, Bioactive glass nanopowder and bioglass coating for biocompatibility improvement of metallic implant, *J. Mater. Process. Technol.* 209 (2009) 1385–1391.
- [14] Q. Chen, I.D. Thompson, A.R. Boccaccini, 45S5 Bioglass-derived glass-ceramic scaffolds for bone tissue engineering, *Biomaterials* (2006) 2414–2425.
- [15] C. Schausten, D. Meng, R. Telle, A.R. Boccaccini, Electrophoretic deposition of carbon nanotubes and bioactive glass particles for bioactive composite coatings, *Ceram. Int.* 36 (2010) 307–312.
- [16] A. Balamurugan, G. Balossier, J. Michel, M.J. Ferreira, Electrochemical and structural evaluation of functionally graded bioglass-apatite composites electrophoretically deposited onto Ti6Al4V alloy, *Electrochim. Acta* 54 (2009) 1192–1198.
- [17] T. Moskalewicz, S. Seuss, A.R. Boccaccini, Microstructure and properties of composite polyetheretherketone/Bioglass[®] coatings deposited on Ti–6Al–7Nb alloy for medical applications, *Appl. Surf. Sci.* 273 (2013) 62–67.
- [18] D. Zhitomirsky, J. Roether, A.R. Boccaccini, I. Zhitomirsky, Electrophoretic deposition of bioactive glass/polymer composite coatings with and without HA nanoparticle inclusions for biomedical applications, *J. Mater. Process. Technol.* 209 (2009) 1853–1860.
- [19] R. Rojaee, M. Fathia, K. Raeissi, M. Taherian, Electrophoretic deposition of bioactive glass nanopowders on magnesium based alloy for biomedical applications, *Ceram. Int.* 40 (2014) 7879–7888.
- [20] K. Wu, P. Imin, A. Adronov, I. Zhitomirsky, Electrophoretic deposition of poly [3-(3-N,N-diethylaminopropoxy)(thiophen)e] and composite films, *Mater. Chem. Phys.* 125 (2011) 210–218.
- [21] Q. Chen, S. Cabanas-Polo, O. Goudouri, A.R. Boccaccini, Electrophoretic co-deposition of polyvinyl alcohol (PVA) reinforced alginate–Bioglass[®] composite coating on stainless steel: mechanical properties and in-vitro bioactivity assessment, *J. Mater. Sci. Eng. C* 40 (2014) 55–64.
- [22] M. Mehdipour, A. Abdollah, A study of the electrophoretic deposition of bioactive glass–chitosan composite coating, *Ceram. Int.* 38 (2012) 471–476.
- [23] M. Kurek, S. Galus, F. Debeaufort, Surface, mechanical and barrier properties of bio-based composite films based on chitosan and whey protein, *Food Packag. Shelf Life* 1 (2014) 56–67.