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Electrophoretic Deposition of Bioglass/TiO_2 nanocomposite on CP-Ti substrates for Biomedical Applications

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Abstract : A large number of people have been affected due to fracture and other bone related diseases due to ageing, trauma, birth defects etc. Biomedical implants have been traditionally used in the field of orthopaedics to repair or replace the malfunctioning bone, alleviate pain, increase mobility and improve the quality of life of the patients. These implants due to several biological and mechanical factors lead to failure. The success rate of revision surgery is less compare to the primary surgery, the additional pain and the infection caused due to the primary surgery is also non negligible. Surface modifications techniques were extensively employed to address this problem. In the present work, 45S5 nanoBioglass (NBG)/titania (TiO_2) composites were coated on the surface of commercially pure titanium (CP-Ti) using electrophoretic deposition technique (EPD). Optimizing the parameters of the EPD coating is the major task for obtaining a uniform deposition. The effect of six processing parameters such as voltage, deposition time, distance of separation between anode and cathode, particle loading, presence of binder, substrate roughness were studied using Design of Experiment (DOE) approach. It was shown that the three parameters such as quantity of particle loading of NBG/TiO_2 in the electrolyte, voltage applied to the electrode as well as nature of the binder added to the electrolyte affects the formation of crack free, thick, and uniform coating on CP -Ti substrate.

1. Introduction

In the recent years, there is an increase in demand for nanocomposite materials. This is because of tuning the interactions of dissimilar inorganic components at its molecular level to form new and unique functional materials with improved properties. In general, composite material offers lot of benefits in comparison with homogeneous materials. In the field of biomaterials, it is very significant that each constituent of the composite must be biocompatible, and the interface used with the constituent to enhance the property of the composite not be degraded by the body environment. Bioglass 45S5 (45% SiO_2-24.5% NaO-24.5% CaO-6% P_2O_5) coatings have been preferred for its osteoconductive and osteoinductive performance. Also, under *in vitro* and in *vivo* conditions, it forms hydroxyl carbonate apatite (HCA), whose chemical, structural and biological similarity with human bone [1,2]. It also used in dental and orthopedic fields to promote the osteoconductivity bonding of metal implants[3]. Hence, Bioglass coatings are widely used to promote the osseointegration of the implant to the surrounding bone. But, the mechanical properties of Bioglass such as its adhesion, mechanical integrity are very poor. It also has other drawbacks such as low hardness, degradation in acids/basic conditions and incomplete bone growth in wet environment. Hence, in the presence of body fluids and under continuous local loading, there occurs an instability or unsatisfactory performance of the implants and failure will taken place[4]. To overcome these drawbacks a bioceramic/metal oxide or bioceramic/metal combination is preferred[5]. Such composites are expected to have improved mechanical and chemical properties compared to pure bioceramics. Titanium dioxide (TiO_2) is one of the bioactive metal oxide constituents, which helps to enhance the mechanical and chemical property of the Bioglass [6]. When both TiO_2 and Bioglass are present in the nano size, it gives an added advantage to enhance the property of the composite. And also the nanostructured materials with its particle size/grain size lesser than 100 nm can significantly improve the bioactivity of the implant and enhance the osteoblast adhesion. This is because of the collagen matrix, which is the building block of the bone is in the nano regime[7].

In addition to the coating properties, the substrate also plays a major role in biomedical applications. Titanium and its alloys are well proven for its biomedical applications and are extensively used in orthopedic and dental applications because of its superior mechanical, electrochemical and biocompatibility[8, 9]. Currently, CP-Ti is widely used for dental, orthopedic hip and knee replacements. The modulus of CP – Ti (100GPa) is comparable with human bone modulus (10-30GPa)[10]. In addition, this alloy possesses highly biocompatible but as per the thumb rule of coatings, the substrate has not produced any change in the coating. But, in heavy loading bone replacements such as hip and knee replacements high bone modulus material with soft coating is always preferable for higher stable osseointegration applications.

Electrophoretic Deposition (EPD) coating is a colloidal process wherein materials are coated directly from a stable suspension by a DC electric field. It is an effective method to fabricate ceramic coatings from powder suspensions. It is also an attractive technique for nanostructural depositions from colloidal solutions because of its high homogeneity. The greater advantages for EPD are less time consumption, perfect coatings, less expensive and to obtain complex shapes [10, 11]. The major problem in EPD coating is optimizing the conditions for coatings. The parameters such as voltage, deposition time, distance of separation between anode and cathode, particle loading, presence of binder, dispersant, substrate roughness, sintering temperatures etc., play a major role in optimizing the coatings. Usually a trial and error approach is done elsewhere for obtaining the coatings. But it is very tedious and the repeatability is also less. In our present work, we focused on "Design of Experiments (DOE)" for obtaining the optimization conditions for Bioglass/TiO_2 composites coatings using EPD technique. The surface roughness, morphology and functional properties of the nanocomposite coatings were also analyzed.

2. Experimental procedures

2.1 Design of Experiments

The parameters chosen for DOE are voltage, deposition time, distance of separation between anode and cathode, particle loading, presence of binder, substrate roughness. These six parameters are set under 2-3 levels based on the maximum and minimum limitations of variation in each. Table 1 gives the details for the levels of parameters for DOE. The weight of the substrate is weighed before and after the coating and the weight gain in the coating is also recorded. The expected outcomes are

(i) Increase in weight of deposition (thick coating),
(ii) No crack in the coating, and
(iii) Uniform coating

From the list of parameters and levels given in Table 1, an initial 16 trial condition has set by random choosing method. Each trial conditions were repeated twice to see the repeatability of the coatings. The weightage percentage for each trial has been given based on our expected outcomes. And the error percentages for each outcome were also calculated using ANOVA method and the optimization condition was achieved. For DOE, CP-Ti substrates of size 10 mm X 10mm X 1mm were sampled and polished from 220# grit to 1600# and mirror polished using 0.3µ alumina powder were used.

Table 1: Levels of variation in parameters for Design of Experiments using EPD coatings

S.No	**Parameters**	**Level 1**	**Level 2**	**Level 3**
1	**Voltage**	30	60	90
2	**Deposition Time**	1 min	3 min	6 min
3	**Distance between anode and cathode**	1 cm	2 cm	-
4	**Particle loading**	0.1gm/10ml	0.2gm/10ml	-
5	**Binder**	PVB	PVA	PEG
6	**Roughness**	Upto 1600 grit	Upto mirror polishing	-

NanoBioglass for the present work was prepared by wet chemical method, that we have already reported[12]. TiO_2 nanoparticles were synthesized by the sol-gel technique through an alkoxide reaction between titanium tetra isopropoxide (TTIP) and Glacial Acetic acid in the presence of double distilled water as a solvent. 4.6 mL of TTIP was added to 9.8 mL of glacial acetic acid under vigorous stirring and thereafter 100 mL of water was added drop wise to get a transparent solution. The solution left for 24 h under continuous stirring to form a gel and dried at 60 ℃ to obtain the nanoparticles of TiO_2.The OH was removed using this heat treatment and leaving behind TiO_2. The obtained TiO_2 powders were characterized using XRD to determine the phases, size and compounds present.

2.2 Nanocomposite and microcomposite TiO_2 / Bioglass coatings

The polished CP-Ti substrate was ultrasonicated in acetone for 30 mins and dried in hot air dryer before used for coatings. Nano TiO_2 and Bioglass powders were loaded in the ratio of as per the trial conditions with isopropyl alcohol as the solvent medium and stirred using magnetic stirrer for 2 h and followed by ultrasonicated for 30 mins. This solution was used as electrolyte for the coatings. To achieve densification in coating, the sintering process was carried out at the heating and cooling rate of 10˚C/min up to 650˚C with and maintained for 2 h. The crystallinity of the nanocomposite coating was investigated by powder X-Ray diffraction (XRD, PANalytical) with monochromotized Cu Kα radiation (λ=0.1548 nm) scanning from 0˚ to 80˚ at the scanning speed of 0.5°/min. The morphology of the coated samples were observed using field emission scanning electron microscopy (FESEM, SU6600 Hitachi) and the elemental confirmation was done using elemental dispersive spectroscopy (EDS, EMAX Horiba).

3. Results and Discussions

3.1 Design of experiments (DOE)

3.1.1 Sampling of trial condition for EPD

The trial condition is set for narrowing of experimental condition using sampling technique with the help of Analysis of Variance (ANOVA). If we have carried out the experiment for all the parameters with all the level of conditions, it might have end up with more than 100 experimental conditions. Herein, by the application ANOVA the parameters were selected to 16 trial conditions. At the end of the experiments each trial is given weightage depends on the basic of the expected outcome such as weight loaded after deposition, coating uniformity and crack formation. In which for crack formation it is given in such a way that, lesser the crack formation, more weightage is given. Table 2 displays the complete details of trial condition selected as per ANOVA by selecting the three levels (level 1, level 2 and level 3) mentioned in table 1. The weightage percentage is given in table 3 for various coating conditions based on the outcome of the coating conditions of Table 2.

Table 2: Trial conditions obtained as per the ANOVA.

Trial Condition	Voltage	Deposition Time	Distance between anode and cathode	Particle loading	Binder	Roughness
1	1	1	1	1	1	1
2	1	2	1	1	2	2
3	1	3	2	2	3	2
4	1	1	2	2	1	1
5	2	1	1	2	3	1
6	2	2	1	2	1	2
7	2	3	2	1	1	2
8	2	1	2	1	2	1
9	3	1	2	1	1	2
10	3	2	2	1	3	1
11	3	3	1	2	2	1
12	3	1	1	2	1	2
13	1	1	2	2	2	2
14	1	2	2	1	1	1
15	1	3	1	1	1	1
16	1	1	1	1	3	2

Table 3: Inference and weightage percentage of the outcome of the trial.

Trial condition	Binder	Trial 1	Trial 2	Inference	percentage of weightage		
					Weight loaded	Coating uniformity	Crack
1	PVB	0.001	0.002	Very thin layer coating	40	20	25
2	PVA	0.0075	0.0082	Found cracks after coating	70	40	20
3	PEG	0.0012	0.0012	Very thin layer coating	45	40	40
4	PVB	0.0011	0.0011	Very thin layer coating	40	30	40
5	PEG	0.0021	0.0073	Coating is non uniform	50	35	30
6	PVB	0.0071	0.0036	Coating is thick only at the bottom	50	20	40
7	PVB	0.0012	0.0007	Very thin layer coating at the bottom	40	20	30
8	PVB	0.002	0.0025	Very thin layer coating at the bottom	45	20	30
9	PVB	0.0013	0.0012	Thin layer coating at the bottom	40	20	30
10	PEG	0.0058	0.0061	Coating in non uniform	55	30	40
11	**PVA**	**0.034**	**0.034**	**Uniform and thick deposition**	**100**	**90**	**80**
12	PVA	0.002	0.002	Very thin perfect coating	60	100	100
13	PVA	0.0034	0.0018	Perfect uniform coating	80	90	90

14	PVB	0.0019	0.0018	Very thin coating	45	20	30
15	PVB	0.0014	0.0004	Very thin coating and coating only at the bottom	35	20	30
16	PEG	0.0013	0.0016	Thin layer coating and coating is non uniform	45	35	40

3.1.2 Error Analysis from trial conditions:

Error analysis is measured using ANOVA for all the three expected outcomes and it is given in Table 4. From the table, we can notice that the error is maximum for particle loading, binder and the voltage, which means that these three parameters play a vital role to achieve the optimization condition for the three expected outcomes. Further, the other three parameters such as deposition time, distance of separation between anode and cathode and surface roughness did not contribute any significant change in the EPD coatings.

Table 4: Error analysis from trial conditions

S.No	Parameters	Error %		
		Uniform coating	Weight of Deposition	Crack free surface
1	**Voltage**	19.498	11.950	16.267
2	**Deposition Time**	2.563	0.0000	0.241
3	**Distance between anode and cathode**	2.381	3.090	0.000
4	**Particle loading**	24.013	11.881	26.386
5	**Binder**	15.874	50.686	1.099
6	**Roughness**	3.041	0.000	1.489

3.1.3 Optimization Conditions and fitted results:

From the error analysis the optimization condition is obtained to minimize the error of voltage, particle loading and binder. For which the voltage is set as 90±10V, particle loading 0.2gm (TiO_2) + 0.2gm (Bioglass)/10ml, binder is chosen as PVB and the loading weight is 0.05±0.01gm/10ml. Four trials were taken by varying these three conditions and the final results are given in Table 5, which resulted the best fitted parameters for high weight of deposition, crack free surface and uniform coating deposition.

Table 5: Fitted parameter conditions for perfect TiO_2/Bioglass EPD coating

Parameters	**Fitted condition**
Voltage	90V
Deposition time	1 min
Distance between anode and cathode	1 cm
Particle loading	0.2gm(TiO_2)+ 0.2gm(HAp)/10ml
Binder	0.05gm/10ml
Polishing the substrate	up to 1600 grit

3.2 Surface morphology and elemental confirmation

The surface morphological and elemental confirmation of TiO_2/Bioglass coating is given in Figure 1. It was found to be a non-homogenous formation of material, and this might be due to heavy particle loading during the coating and sintering processes. This non-homogenous coated enhances the surface roughness of the coating, where the higher surface roughness and the presence of nanoparticles facilitates higher cell proliferation and higher rate of osseointegration[13]. The elemental analysis further confirms the presence of elements such as Na, Ca, P, Si and O in the coated samples and Ti in the substrate.

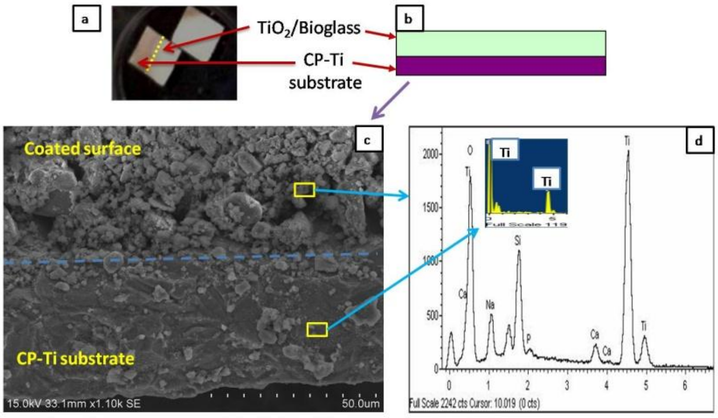

Figure 1: (a) EPD coated sample, (b) Schematic illustration of coating on CP-Ti substrate, (c) Cross-section FESEM image of CP-Ti coated TiO_2/Bioglass, (d) Elemental confirmation of the composites.

3.2 Crystal structure analysis

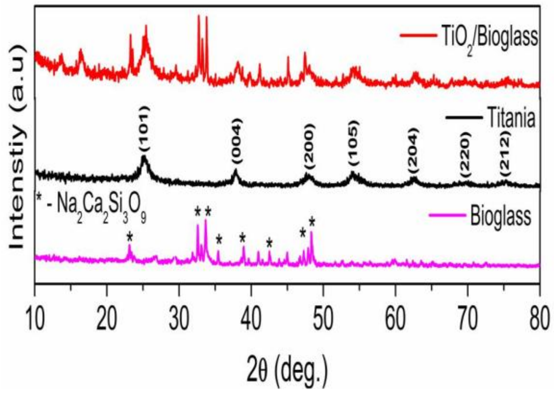

Figure 2: X-ray diffraction spectra of Bioglass, TiO_2 and TiO_2/Bioglass nanocomposites.

The XRD analysis of 45S5 nanoBioglass (NBG)/titania (TiO_2) composites coating along with the pure TiO_2 and Bioglass nanopowders are shown in Fig. 2. The XRD pattern that was obtained in pure Bioglass samples depicted a phase that had a close similarity to sodium calcium silicate $Na_2Ca_2Si_3O_9$ (JCPDF# 45-0550),[14,15,16] which is a highly bioactive crystal phase of interest in this present study. The presence of this peak also enhances the mechanical properties of the Bioglass composites. The titania peak is similar to the anatase crystal structure and well matched with the JCPDS # 21–1274. The broad peak of TiO_2 shows a smaller crystallite size of the material. From the Scherrer formula, the crystallite size of the TiO_2 nanoparticles is found to be 4 nm. The anatase titania coating on CP-Ti surface improves the osseointegration in *in vivo*, [17], leads to a higher antibacterial efficacy [18] and also enhances the biological genetic effects [19.]

Conclusion:

45S5 nanoBioglass (NBG)/titania (TiO_2) composites was coated on CP-Ti substrate using electrophoretic deposition technique. The effect of six processing parameters such as voltage, deposition time, distance of separation between anode and cathode, particle loading, presence of binder, substrate roughness were studied using DOE approach. Optimization was performed based on Analysis of Variance method. It was shown that the three parameters such as quantity of particle loading of TiO_2/Bioglass in the electrolyte, voltage applied to the electrode and nature of the binder added to the electrolyte effects the formation of uniform, crack free and thick coating of nanoceramic TiO_2/Bioglass on CP -Ti substrate. The nanocomposite coatings on different Ti substrates were further investigated by XRD, FESEM and EDS analysis, which were confirmed that the substrate does not induce any change of crystallinity or phases in the composite coatings. From the osseointegration perspective of view, the nanocomposites coating of TiO_2/Bioglass will certainly increase the mechanical and osseointegration property of the implant to the surrounding bone.

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