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Tailoring the surface characteristics of electrophoretically deposited chitosan-based bioactive glass composite coatings on titanium implants via grit blasting

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ABSTRACT

Chitosan, chitosan/45S5 bioactive glass (mBG), chitosan/nanobioglass (nBG), and chitosan/mBG/nBG coatings were deposited on grit-blasted and mirror-polished Ti6Al4 V alloy substrates by electrophoretic deposition (EPD). This study discusses how the surface characteristics of the substrates influence the 3D surface topography, areal surface roughness, morphology, and wettability of chitosan-based thin composite coatings while focusing on tuning the surface characteristics by grit-blasting. The surfaces of coated and uncoated specimens were characterised by SEM analysis with EDX, image analysis, contact angle measurements, 3D surface topography analysis, FTIR analysis, and *in-vitro* bioactivity studies. The coatings deposited on grit-blasted substrates presented rougher surface topography, higher areal surface roughness values and wettability compared to the mirror-polished surfaces. A deposition mechanism was suggested to clarify the deposition of chitosan/mBG coatings on grit-blasted substrates. Apatite crystals were formed on chitosan/mBG coatings after immersion in SBF for three days. A robust image analysis method was applied to reveal the distribution and area coverage percent of deposited mBG, which demonstrated the increase of mBG coverage with the increases in voltage. The present study shows that grit blasting could be a favourable surface treatment to tailor the surface characteristics of organic-inorganic composite coatings by influencing their surface topography, roughness, and wettability.

1. Introduction

Titanium alloys are among the most widely used metallic implants in orthopaedic and dental applications owing to their high strength-weight ratio, excellent corrosion resistance, and biocompatibility [1–6]. Ideal implants should possess enhanced adhesion to the human tissue along with bioactivity, antibacterial activity, and improved corrosion resistance to prevent the implant failures due to bacterial infection, lack of bioactivity, and loosening [1–4,7–10]. These properties could be improved by either the modifications such as surface roughness and wettability or by the deposition of bioactive and antibacterial coatings [11]. Bioactive coatings such as hydroxyapatite (HA), bioglass (BG), and biopolymer [5,12–14] have been deposited to improve the bone integration between the metallic implants and the human tissue [13,15] by various deposition methods [3,8,16].

Electrophoretic deposition (EPD) is a versatile method to produce polymeric, ceramic coatings and their composite coatings on titanium alloys for biomedical applications [3,16]. EPD is defined as the deposition of suspended particles under an electric field between two electrodes [17,18]. The key features of EPD are the use of low cost equipment [19], short processing time [13], high processing efficiency [20], deposition of homogeneous coatings with high purity [11,17,19], deposition on complex shaped substrates [13,19,21,22], deposition of coatings with interconnected porosity for enhancing bone ingrowths into the porous coatings [12,20,21], controllability of coating thickness [22,23], and deposition at room temperature [19]. EPD allows the co-

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deposition of polymers and ceramics that can be used to produce biomedical coatings [12,21,22,24,25].

Chitosan contributes to the elimination of sintering process [12] and allows the co-deposition of inorganic particles with EPD. It is a natural, biodegradable, biocompatible [11], non-toxic, bio-functional [26] biopolymer for drug delivery systems and tissue engineering [12,26,27], which can accelerate wound healing [10,27,28] owing to its improved cellular attachment and antibacterial effect [13]. The other promising features of chitosan can be summarised as its moderate chemical [12] and corrosion resistance [29], good thermal stability [30], moderate mechanical properties [18], low-cost [22], and capability to form different shapes of films with EPD [10,17,18,21,31]. Chitosan coatings have been therefore deposited by EPD for a great variety of applications ranging from skin, bone, cartilage, and vascular grafts to substrate for cell culture [26]. There has been an increasing interest in utilising chitosan for the surface coatings of orthopaedic implants over the last years [13].

In general, the surface characteristics and the related biological performance of biomedical coatings strongly depend on the applied coating method and the composition of the coatings. Apart from these, the surface morphology, topography, roughness, and wettability of the coatings play an essential role in their mechanical and biological performance [12,17,20,22]. The surface roughness of chitosan-based composite coatings has been investigated briefly, and the importance of surface roughness on the coating performance has been underlined in the existed literature [11,12,16,18,22,32–35]. For instance, it was stated that the antibacterial effect of chitosan/BG composite coatings relied on the roughness of the coating and the higher surface roughness increased the chance of bacterial growth [22]. Besides surface roughness, wettability is another surface characteristic, which affects the biological properties [19] and it is substantially related to surface roughness [36–39]. Nevertheless, the correlation between surface roughness and wettability is quite complicated [40] as many factors such as the hardness, chemical properties, and microstructure of surface influence the wettability [41]. The surface characteristics of metallic substrates also affect the resultant surface characteristics of the coatings, e.g. roughness, wettability, and specifically the adhesion to the substrate [42–44]. However, there are limited studies available dealing with the wettability of chitosan-based composite coatings deposited by EPD [11,33,34,45].

Grit blasting is a useful mechanical surface treatment owe to its simplicity and low cost [46] and is widely used to clean and roughen up the surfaces of substrates prior to coating process to enhance the adhesion between the substrate and the coating [43,47–52]. Abrasive particles such as alumina [43], garnet [53], and SiC [46] are accelerated by means of compressed air through a nozzle and repeatedly impacted onto the surfaces of substrates to modify surface characteristics during grit blasting [47]. Grit blasting may enhance the osteointegration of uncoated implants [49,54] and improve the bone-to-implant contact area [47,50], cell adhesion [55,56], and the adhesion strength of coatings [43]. However, the effects of substrate surface characteristics on the surface topography and wettability of electrophoretically deposited chitosan coatings have not been clarified yet. The present study investigates the effects of the substrate surface characteristics on the final surface properties of the electrophoretically deposited chitosan-based composite coatings. It aims to produce thin coatings to maintain the beneficial surface features of the grit-blasted substrates and to underline the importance of grit blasting on the surface characteristics of chitosan-based composite coatings. It would pave the way for further utilisation of grit blasting to tailor the surface properties of electrophoretically deposited coatings for various applications.

Table 1
Chemical composition and physical properties of BG particles used in the study.

Vitryxx® Bioactive Glass (Bioactive glass® 45S5)			
Composition in wt%			
SiO_2	CaO	Na_2O	P_2O_5
45 ± 5	24.5 ± 3	24.5 ± 3	6 ± 2
Physical properties			
Grain size d50 (μm)		Grain size d_{90} (μm)	
2.0 ± 1,0		< 20	
Nanobioglass (Shott NF180 glass)			
Composition in wt%			
Al_2O_3	B_2O_3	BaO	SiO_2
10	10	25	55
Physical properties			
Grain size d50 (nm)		Grain size d_{90} (nm)	
180 ± 30		< 500	

2. Experimental

2.1. Materials

The most commercially used titanium alloy, Ti6Al4V, was chosen as the substrate material and was supplied in the form of 100 × 100 cm sheets with a thickness of 2 mm. The sheets were cut to specimens of 76.2 × 25.4 mm by using a precision laser cutting, and then the specimens were ultrasonically cleaned for 30 min before the mechanical surface treatments. The chemical composition, mechanical, and physical properties of the alloy were given in elsewhere [57].

For the EPD of chitosan-based coatings, medium molecular weight chitosan (MW = 80 kDa, Sigma-Aldrich) with a degree of deacetylation of around 85% was used. Two different types of BG particles, namely Vitryxx® Bioactive Glass, also commercially known as 45S5 bioactive glass (mBG), and nanobioglass (nBG) were used (SCHOTT AG, Germany). The chemical compositions and physical properties of the BG particles are given in Table 1.

2.2. Mechanical surface treatments

In the present study, mirror-polished and grit-blasted substrates were prepared by metallographic preparation and grit blasting, respectively. The metallographic preparation was carried out by grinding the substrates with 100, 320, 600, and 1000 grit meshes and polishing with 9 μm and 1 μm diamond paste with a grinding and polishing instrument (Struers, Germany) and then the specimens were ultrasonically cleaned with ethanol for 15 min at room temperature.

The grit-blasted substrates were prepared by using a custom-design grit blasting instrument. Sharp-edge alumina (Al_2O_3) particles (Fig. 1)

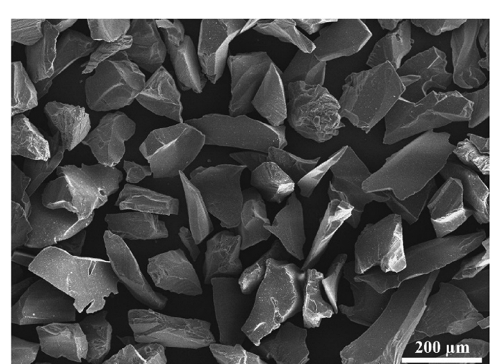

Fig. 1. SEM image of the erodent particles used in the present study.