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Orthopaedic bioactive glass/chitosan composites coated 316L stainless steel by green electrophoretic co-deposition

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ABSTRACT

Single-step electrophoretic co-deposition (EPD) technique was used to enhance the bioactivity of the 316L stainless steel (316L SS) surface by bioactive glass/chitosan composite coatings. Two modified glass compositions of Bioglass® by the addition of boron were utilized to prepare such composite layers, and the Bioglass® was synthesized for comparison. Different EPD coating factors were studied. Namely, voltage, time, glass powder, and chitosan concentrations, to obtain crack-free and good adhesive coatings. The achieved surfaces were characterized by SEM/EDX, TGA, XRD and FTIR and their wettability and roughness were investigated. The in vitro bioactivity of the coated metals was compared in simulated body fluid (SBF) and Dulbecco's modified eagle medium (DMEM) for up to 15 days. The electrochemical corrosion behavior of the coated metals was evaluated using potentiodynamic polarisation and impedance techniques in the two biological solutions SBF and DMEM at 37 °C. The results showed that the achieved coatings were uniform, homogenous and crack-free with desirable thickness. Moreover, the coating layers were exhibited by very high wettability, and their roughness values ranged from 170 ± 18 to 234 ± 17 μm. The in vitro bioactivities proved that the coating layers represented a better ability to form hydroxyapatite crystals on their surfaces in SBF than in DMEM. The corrosion resistance of 316L SS was improved by the bioactive composite coatings.

1. Introduction

Interest significantly increased in the field of coating of metallic implants by bioactive materials. Widely used implants for orthopedic purposes are made mainly of metal alloys, such as stainless steel and titanium alloys. Importantly, 316L stainless steel has been used extensively in the orthopedic field. It is due to its high mechanical strength and low price. Despite the advantages of such metal alloy, it has a shortage in implantation field. Some toxic ions may be released into the body from the metal surface, and the metal is likely encapsulated by fibrous tissue [1,2], which could lead to the movement and loosening of the metal implant [1,3]. Nevertheless, a coating of the metal implant surface with bioactive materials has been applied as a practical solution for these problems. Such bioactive layers are characterized by their ability to induce osteointegration of the metal surface, as well as, decreasing or even suppressing the ions released from the metal.

There have been numerous bioactive materials used as coatings for metal implants, such as hydroxyapatite (HA) [4–6], bioactive glass and glass-ceramic [7–10] and composite materials based on biopolymers and ceramic materials [11–14]. Recently, composite inorganic-organic materials have attracted the interest in the orthopedic field. Such materials mimic the bone structure which is composed of collagen as organic phase and nano-HA crystals as the inorganic phase [15]. Therefore, the composite coatings based on biopolymer (as the organic phase, e.g., alginate and chitosan) and ceramic particles (as inorganic phase, e.g., HA and bioactive glasses) combine the bioactivity of the ceramic component and the mechanical properties of the polymer [16]. Furthermore, active biomolecules, such as antibiotics, proteins, and enzymes can be included throughout the polymer matrix during the coating process [16,17]. Moreover, a room temperature coating process can be achieved by the use of a polymer phase.

Bioactive glasses are an essential class of material for biomedical applications. They can form a chemical bond with surrounding tissue

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via the formation of HA layer. The bioactive glass was initially discovered by Hench and coworkers in the late 1960's and early 1970's, which was encoded later as 45S5 or Bioglass® [18]. A new research field for using glasses as implants and bone tissue engineering applications was established. After Hench's glass, other types of bioactive glasses were developed and used in different biomedical applications. Such glasses were widely utilized as bioactive coatings for metal implants. Depending on preparation method, two types of bioactive glass used as a bioactive coating of different metal surfaces; melt-derived bioactive glasses [8,19–21] and sol-gel-derived bioactive glasses [22–27]. Nevertheless, the incorporation of boron in bioactive glass compositions proved to enhance the bioactivity and biocompatibility of the glass. Boron showed a potential effect on stimulation angiogenesis in vivo [28], as well as, it proved that it enhanced the growth of bone tissue [29,30]. Moreover, it was confirmed that boron compounds demonstrated powerful anti-inflammatory effect with minimum side effects [31]. These anti-inflammatory influences come from the defeat of serine proteases that are released by inflammation-activated white blood cells. As well as, boron-containing compounds can reduce the reactive oxygen species which produced in the course of neutrophil's respiratory burst along with T-cell activity [29,31]. Consequently, the incorporation of boron in bioactive glasses is of particular interest for biomedical applications.

Biopolymers showed a substantial impact on the enhancement of composite coatings properties. Different types of biopolymers were used with bioactive glass particles for coating purpose of metal implants. e.g., polyetheretherketone polymer utilized with 45S5 glass as a composite coating on shape memory alloy (NiTi, Nitinol®) [32]. Furthermore, bioactive glass-alginate composite coatings have been investigated for metal coating application [33]. Moreover, different composite layers based on bioactive glass particles and chitosan have been studied [25,34–38].

Chitosan has been widely used as an organic component of organic-inorganic composite coatings. It is a natural cationic polysaccharide polymer derived from chitin, which is the second most abundant natural polymer after cellulose. It has numerous advantages to be used in different biomedical applications, such as its antibacterial properties [39]. Additionally, it represented cytocompatibility with varying types of cells [40]. Moreover, desirable mechanical strength, biocompatibility, and biodegradability of chitosan are beneficially controllable [41].

The process of organic-inorganic coatings is a room temperature technique. Following this concept electrophoretic deposition (EPD) in the aqueous electrolyte is considered a superior and green route in this regard. It is characterized by its simplicity being cost-effectiveness with short processing time and achievement of uniform coatings with the possibility for a coat of complex shapes. The EPD process is carried out by passing an electric current between two conductive electrodes immersed in a colloidal suspension. Under an electric field, the particles are charged and moved to the oppositely charged electrode to deposit and co-deposit achieving an adhesive layer on the surface of such electrode [42–45]. EPD technique has been successfully used to produce composite coatings based on bioactive glass and biopolymers for orthopedic and dental application [32,34–36,46].

The present work aimed to prepare composite coatings for 316L SS based on chitosan and new glass compositions using the simple and cost-effective eco-friendly EPD method. The new glasses contained boron were prepared. Nevertheless, it was targeted to tailor different properties of the suggested composite coatings by changing glass compositions and glass to polymer ratio. Moreover, the surfaces acquired the advantage of chitosan, such as antimicrobial activity, enhancement of the coating adhesion on the metal. Finally, the electrochemical tests of different coated metallic substrates were performed to determine the corrosion behavior of such samples.

Table 1
Three different glass compositions (wt%) used in this study.

	SiO_2	Na_2O	CaO	B_2O_3	P_2O_5
40S	40.0	25.0	20.0	5.0	10.0
HB5	40.0	24.5	24.5	5.0	6.0
H	45.0	24.5	24.5	–	6.0

2. Experimental procedures

2.1. Materials

The following chemicals with high purity were used in the present work. Chitosan with high molecular weight, 310–375 kDa (Sigma-Aldrich), acetic acid (98%) (Acros Organics, Belgium), SiO_2 (99.8%, quartz sand, Egypt), Na_2CO_3 (99.5%, ADWIC, Egypt), $CaCO_3$ (98.5%, BDH, UK), H_3BO_3 (99.5%, ADWIC, Egypt) and $NH_4H_2PO_4$ (ARABLAB Company, UAE) to fabricate glasses and composites coatings.

2.2. Synthesis of bioactive glass

Table 1 represents glass compositions used in this work in weight percents. Bioglass® (45S5) was synthesized in parallel for comparison. High purity chemicals, SiO_2, Na_2CO_3, $CaCO_3$, H_3BO_3, and $NH_4H_2PO_4$, were used as glass precursors. Glass batch components were mixed well to ensure powder homogeneity. To get rid of the gases resulting from heating the glass components at a temperature above 600 °C the mixed powders were transformed to a platinum crucible and heated to 1000 °C in a muffle furnace for 1 h. After that, the glass batch was melted at temperature range 1350–1450 °C. The molten glass was poured into water to achieve glass frits. These frits were ground in a ball mill and sieved to get particle sizes < 63 μm. Moreover, the particle size distribution and zeta potential were evaluated for the achieved glass grains in an aqueous medium using dynamic light scattering analysis (Nicomp N3000 particle size analyzer, Santa Barbara, Calif., USA). The particles were dispersed in the water by sonication probe before the measurement.

2.3. EPD coating process

A high molecular weight chitosan polymer (0.5, 1.0 or 1.5 g) was dissolved in 1000 ml of 1% acetic acid (98%) solution for one day at room temperature. After complete dissolution of the polymer, glass particles were suspended in the solution by stirring for 2 h and sonication (WiseClean, WUC-D03H) for 15 min. Additionally, pH of suspensions was measured.

Stainless steel 316L electrode plates (15 × 10 × 0.2 mm) were polished by 600 and 1200 silicon carbide paper and washed with distilled water and acetone in an ultrasonic bath for 15 min and dried immediately before the electrophoretic coating process. The two electrode coating cell was composed of stainless steel anode and cathode with 1 cm distance with subjected coating area of 10 × 10 mm. Then the two electrodes were immersed in the glass suspension, and an electric voltage was applied by DC power supply (GW Model No: GPC-3060). The samples were carefully and slowly pulled out from the suspension after EPD. Finally, the samples were dried at least for 24 h at ambient conditions.

Different parameters were applied to achieve the optimum conditions for the electrophoretic deposition process. Such parameters for coating were applied voltages (20, 30, 40 and 50 V), time (3, 5, 7, 10 and 15 min.), glass concentrations (2, 4, 6 and 8 g/l), and chitosan concentrations (0.5, 1 and 1.5 g/l). The wt% of the polymer in the composite coating can be calculated from the following Eq. (1):

$$\text{Polymer wt\%} = Wp^{*}100/(Wp + Wg) \quad (1)$$