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Electrophoretic deposition of hydroxyapatite nanoparticles in different alcohols: Effect of Tris (tris(hydroxymethyl)aminomethane) as a dispersant

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Abstract

The suspensions of HA nanoparticles (20 g/L) in different alcohols (methanol, ethanol, isopropanol and butanol) were prepared and Tris (tris (hydroxymethyl)aminomethane) was used as a dispersant to enhance their colloidal stability. It was found that H^+Tris ions generated through the Tris protonation in the alcoholic suspensions are chemically adsorbed on the HA nanoparticles *via* hydrogen bonding with their surface P–OH groups increasing their zeta potential and so their colloidal stability. It was found that the higher the molecular weight of alcohol the lower the concentration of generated H^+Tris ions in them; so the higher concentration of Tris should be added into them to saturate the surface of HA nanoparticles with H^+Tris ions leading to the higher amounts for optimum concentration of Tris in them. Electrophoretic deposition (EPD) was performed at 60 V for different times. EPD kinetics was the fastest from the suspensions with optimum concentration of Tris due to the highest zeta potential and so the highest mobility of particles in them. The coatings deposited from the suspensions with optimum concentration of Tris had the uniform, fine and agglomerate-free microstructure; so these coatings can act as the effective barrier against the corrosive fluid to reach the substrate surface leading to the higher reduction in corrosion rate of substrate.

Keywords: Electrophoretic deposition (EPD); Hydroxyapatite (HA) nanoparticles; Tris (tris(hydroxymethyl)aminomethane); Alcohol; Coating

1. Introduction

Hydroxyapatite (HA: $Ca_{10}(PO_4)_6(OH)_2$) is the major inorganic component of human bone and teeth [1]. Due to its high biocompatibility, bioactivity, biodegradability and osteoconductivity, HA has been used extensively in orthopedic biomedical applications [2–4]. Unfortunately, HA has poor mechanical properties such as low fracture toughness and brittleness restricting its use in load bearing clinical applications. One solution to this problem is the application of HA as a coating on the metallic implants such as 316 L stainless steel, titanium and its alloys; this combines the high mechanical properties of metal with the excellent biocompatibility and bioactivity of HA. Several coating methods have been used to deposit HA coatings on the metallic substrates such as sol–gel [5,6], thermal [7] and plasma [8] spraying, electrolytic deposition [9], biomimetic formation [10], sputtering [11] and so on. Among these methods, plasma spraying is the most developed technique for depositing the HA coatings; however, this process needs high cost equipment and is a line-of-sight process restricting the application of uniform coatings on the implants with complex shapes. Another technique that has recently attracted increasing interest in the depositing of HA coatings on metallic substrates is electrophoretic deposition (EPD) [12–17]. EPD is a two-step process: in the first step the charged particles dispersed in a suitable liquid migrate toward the oppositely charged electrode (substrate) under an applied electric field; in the second step they deposit on it and form a compact particulate layer there [18]. EPD has several advantages such as simplicity, need to low cost equipment, short formation time, deposition of even coating on the substrates with complex geometries and the ability to control the microstructure of deposit by simple adjustment of EPD parameters such as deposition voltage and time [18]. Another specific and important advantage of EPD is its inherent ability to deposit the HA coatings with interconnected porosity essential for implant fixation in the body by

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bone ingrowths into these pores [16]. The main drawback of EPD like other low temperature colloidal processes is the necessity of subsequent high temperature sintering to consolidate the loosely packed particulate EPD deposits and enhance their adhesion strength to the substrate. The pure HA decomposes to tricalcium phosphate phase at temperature range of 1200–1450 °C [19]; this phase is undesirable since it is biodegradable *in vivo* [20]. When HA is coated on the metallic substrate, the diffusion of metallic ions from substrate into the HA coatings occurs leading to the considerable drop in the temperature range (as low as 900 °C) where its decomposition occurs [20,21]. Moreover high temperature sintering can deteriorate the mechanical properties of underlying metallic substrate. Therefore electrophoretically deposited HA coatings on metallic substrates must be sintered at temperatures as low as possible. It is well known that the nanostructured materials can be sintered at lower temperatures than conventional microstructured counterparts. EPD has been used extensively to deposit nanostructured coatings from the suspensions loaded with nanoparticles. However, due to the very large specific surface area, nanoparticles exhibit high tendency to stick together and form coarse agglomerates especially in non-aqueous suspensions (due to their low dielectric constant leading to the small zeta potential of particles in them) commonly used in EPD. So in order to deposit nanostructured HA coatings with uniform, fine and agglomerate-free microstructure and so high sinterability, the addition of an effective dispersant into the suspension to prevent the agglomeration of nanoparticles is necessary. Usually high molecular weight polyelectrolytes are added to non-aqueous suspensions to increase their colloidal stability by electrosteric stabilization mechanism [22–26]; however, the addition of polyelectrolytes into the EPD suspensions increases their viscosity leading to lower EPD kinetics from them and also introduces large amount of polyelectrolyte macromolecules as the impurity into the composition of deposited coatings which can deteriorate their properties. So the finding and using the appropriate low molecular weight electrostatically stabilizer dispersants is of great importance in the EPD processing of nanostructured coatings from non-aqueous suspensions. These dispersants can ionize and be adsorbed on the surface of nanoparticles to enhance their surface charge (zeta potential) and so colloidal stability. In this work the Tris (tris(hydroxymethyl)aminomethane ($H_2NC(CH_2OH)_3$)) with the molecular weight of 121.14 g/mol was used as a additive to disperse HA nanoparticles in different alcoholic suspensions; it was found that Tris is an effective dispersant for the stabilization of HA nanoparticles in different alcoholic suspensions. The mechanism of Tris action as a dispersant for HA nanoparticles in alcoholic suspensions was investigated; the effect of Tris on the EPD of HA coatings and their properties was also studied.

2. Materials and method

2.1. Suspension preparation

Hydroxyapatite nanoparticles were synthesized by wet chemical method [27]. The synthesized HA nanopowders were observed by scanning electron microscope (SEM). Tris (Merck, 99.8%) was used as a dispersant to increase the colloidal stability of HA nanoparticles in alcoholic suspensions. Tris was added into different alcohols (methanol (99.99%, Merck), ethanol (99.8%, Merck), isopropanol (99.99%, Merck) and butanol (99%, Merck) at various concentrations and dissolved in them by stirring magnetically for 30 min. Then 20 g/L of HA nanoparticles were added into them and stirred magnetically for 24 h and ultrasonically dispersed for 10 min. The sedimentation test was performed to investigate the effect of Tris addition on the colloidal stability of HA nanoparticles in different alcoholic suspensions. To do this the prepared suspensions (50 mL) were poured into test tubes and allowed to settle in resting condition for 30 days. The electrical conductivity of different alcoholic suspensions was measured against Tris concentration. The zeta potential of particles in different alcoholic suspensions was measured versus Tris content (Malvern instrument, Worcestershire, UK). The dilute samples required for zeta potential analysis were prepared according to Ref. [28]. Fourier transform infrared spectroscopy (FTIR) was used to investigate the adsorption of Tris on the HA nanoparticles. The samples for FTIR analysis were as synthesized HA nanopowder and the ones extracted from the different alcoholic suspensions with Tris additive by centrifuging and drying at 100 °C overnight.

2.2. Electrophoretic deposition

The plates of 316 L stainless steel with the dimensions of 40 mm × 20 mm × 1 mm were used as the cathode (substrates) as well as the anode (counter) electrodes in the EPD cell. The distance between two electrodes was 1 cm in EPD cell. Only 20 mm × 20 mm of electrodes was exposed to suspension in EPD cell and remainder of their surface was insulated by polymeric adhesive tape. EPD was performed at 60 V for different times. The *in-situ* kinetics of EPD as well as the current density during EPD were recorded using the method described in Ref. [29].

2.3. Characterization of coatings

The microstructure of dried and unsintered coatings prepared at 60 V and 20 s from different alcoholic suspensions containing various concentrations of Tris was observed by SEM. The thickness of these coatings was measured by a coating thickness gauges (Qnix 8500, Germany). The dried HA coatings deposited at 60 V for 20 s from different alcoholic suspensions were sintered at 800 °C (heating rate: 5 °C/min) for 1 h under flowing argon gas atmosphere (flow rate: 25 mL/min). The effect of these coatings on the corrosion rate of substrate in the simulated body fluid (SBF) environment at 37.5 °C was studied by potentiodynamic polarization method (EG&G Princeton Applied Research 273A). Tafel analysis was used to determine the corrosion current from polarization curves. SBF was prepared on the base of method proposed in Ref. [30]. A three electrode cell was used for electrochemical polarization studies. Bare substrate as well as HA coated ones were used as the working electrode. A platinum grid and a saturated calomel