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Effect of suspension medium on the electrophoretic deposition of hydroxyapatite nanoparticles and properties of obtained coatings

Morteza Farrokhi-Rad, Taghi Shahrabi*

Department of Materials Science & Engineering, Tarbiat Modares University, P.O. Box 14115-143, Tehran, Iran

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Abstract

The suspensions of hydroxyapatite (HA) nanoparticles were prepared in different alcohols. The zeta potential of HA nanoparticles was the highest in butanolic suspension (65.65 mV) due to the higher adsorption of $RCH_2OH_2^+$ species via hydrogen bonding with surface P–OH group of HA. Electrophoretic deposition was performed at 20 and 60 V/cm for different times. Deposition rate was faster in low molecular weight alcohols due to the higher electrophoretic mobility of HA nanoparticles in them. The coating deposited from butanolic suspension had the highest adhesion strength and corrosion resistance in SBF solution at 37.5 °C. The surface of this coating was covered by apatite after immersion in SBF solution for 1 week.

Keywords: C. Corrosion; Alcohol; Coating; Electrophoretic deposition (EPD); Hydroxyapatite (HA) nanoparticles

1. Introduction

Hydroxyapatite (HA) is the main inorganic part of human bone [1]. HA has good bioactivity, biocompatibility, osteoconductivity and biodegradability so that it has been extensively used in biomedical applications [2–4]. However, HA has poor mechanical properties (such as low facture toughness) limiting its orthopedic applications. So usually it is applied as the coating on the metallic implants such as titanium and stainless steel. Electrophoretic deposition (EPD) has been extensively used to deposit HA coatings on the metallic substrates [5–10]. EPD is a two step process: in the first step charged particles are dispersed in a suitable liquid and migrate towards the electrode with opposite charge under the application of electric field. In the second step, they deposit there and form a relatively dense layer of particles on it [11]. EPD has several advantages such as simplicity, need to low cost equipments, ability to manipulate the microstructure of deposit by the simple adjustment of process parameters such as deposition time, voltage and so on [11]. Due to the particulate nature of EPD it has the ability to deposit the coatings with interconnected porosity appropriate for implant fixation by bone ingrowths into them [12].

The kinetics of EPD follows from the Hamaker equation [13]

$$\frac{dw}{dt} = f\mu cAE \tag{1}$$

Where μ is the electrophoretic mobility of particles, c is the concentration of suspension, A is the deposition area and E is the applied electric field and f is a factor introduced into the equation to take into account that not all the particles brought to the substrate electrode take part in deposit formation. The electrophoretic mobility of particles can be obtained by the following equation [14]

$$\mu = \frac{\varepsilon_0 \varepsilon_r \zeta}{\eta} \tag{2}$$

Where ε_0 is the vacuum permittivity (8.854×10^{-12} F/m), ε_r is the relative dielectric constant of medium, ζ is the zeta potential of particles, and η is the viscosity of medium.

Using water as the suspension medium in EPD is limited due to its electrolysis at relatively low applied electric fields; the water electrolyses generates hydrogen and oxygen gases at cathode and anode, respectively, resulting in the deposits with

*Corresponding author. Tel.: +98 21 8288 3378; fax: +98 21 8288 3381.
E-mail addresses: morteza_farrokhi_rad@yahoo.com (M. Farrokhi-Rad), tshahrabi34@modares.ac.ird (T. Shahrabi).

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poor quality microstructure including pin holes and bubbles [15]. So, non-aqueous solvents such as alcohols are usually used as the suspension medium in EPD [16,17]. In this work the EPD of HA nanoparticles from different alcoholic suspensions (methanol, ethanol, isopropanol and butanol) and the properties of obtained coatings have been investigated.

2. Materials and methods

2.1. Suspensions preparation

Hydroxyapatite (HA) nanoparticles were synthesized by metathesis method [18]. The suspensions of HA nanoparticles (10 g/L) were prepared in methanol (99.99%, Merck), ethanol (99.8%, Merck, Germany), isopropanol (99.9%, Merck, Germany) and butanol (99%, Merck, Germany) by the addition of 1 g HA nanoparticles into 100 mL of alcohols and magnetically stirring them for 24 h. Finally, the suspensions were ultrasonically dispersed for 10 min (Sonopuls HD 3200, 20 kHz; Bandelin Co., Berlin, Germany). The electrical conductivity of the alcohols was measured before and after the addition of 10 g/L HA nanoparticles into them with the accuracy of ± 0.01 μS/cm (Cond 720, WTW series; Inolab, Weilheim, Germany). The zeta potential of HA nanoparticles was measured in different alcoholic suspensions (Malvern instrument, 3000HS, Worcestershire, U.K). The FTIR analysis was used to investigate the adsorption of alcoholic molecules on the HA nanoparticles. The samples for FTIR analysis were prepared by the following method: some powders were extracted from the suspensions by centrifuging (6000 rpm, 15 min) then washed with deionized water (3 times) and dried at 100 °C for 24 h.

2.2. Electrophoretic deposition

Electrophoretic deposition (EPD) was performed using a two electrode cell. Both the working (substrate) and counter electrodes were the plates of 316 L stainless steel with the dimension of 20 mm × 10 mm × 1 mm. Only 10×10 mm^2 of substrates was exposed to deposition and remainder insulated. EPD was performed at 20 and 60 V/cm for different times (30, 120, 240, 360, 480 and 600 s) using a laboratory D.C. power supply (HY30002E; Huayi Electronics Industry Co., Hangzhou, Zhejiang, China). The current density during EPD was recorded by computer connected multimeter (289 True RMS; Fluke, Everett, WA). Deposition rate was studied by weighting the substrate before and after EPD using a 0.1 mg accuracy balance (GR-200; A&D Co., Tokyo, Japan). EPD was performed 3 times for each specimen and the average weight of deposition was calculated.

2.3. Coatings characterization

Deposits were dried at room temperature overnight. The thickness of dried coatings was measured by a coating thickness gauges (Qnix 8500, Germany). Thickness measurement was performed on the 3 specimen and the average

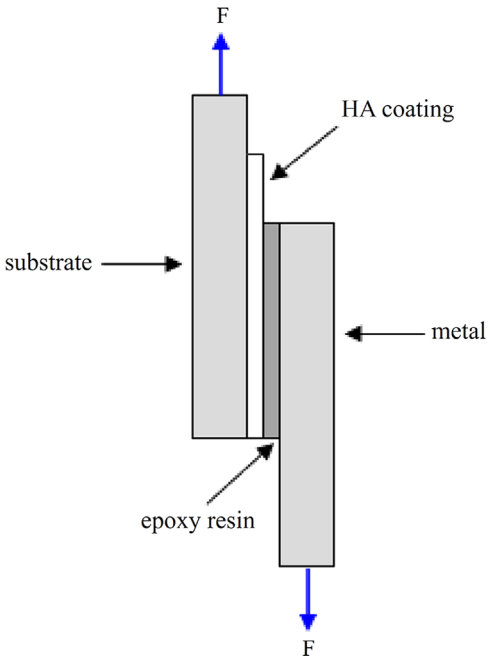

Fig. 1. Schematics of adhesion strength testing of HA coating on 316L stainless steel substrate.

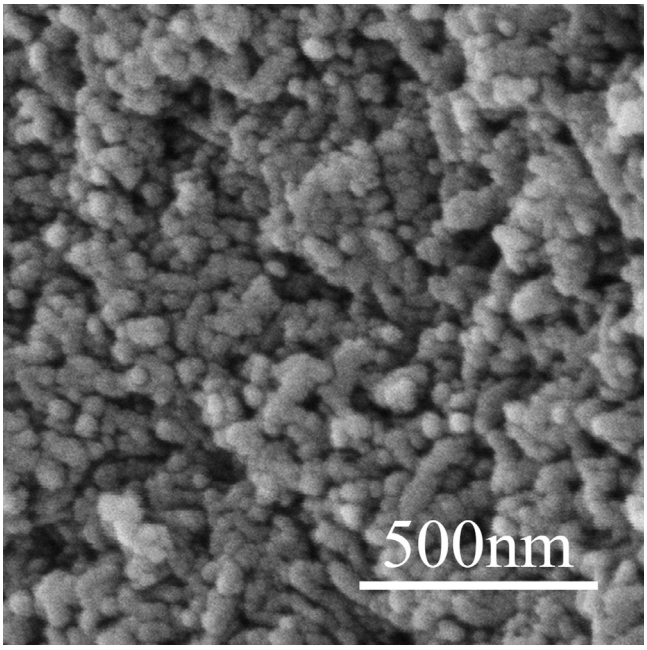

Fig. 2. SEM image of synthesized HA nanoparticles.

Table 1
The values of electrical conductivity of alcohols in the absence as well as the presence of 10 g/L HA nanoparticles.

Type of alcohol	Electrical conductivity (μS/cm)	
	Without HA	With 10 g/L HA nanopowder
Methanol	0.7	3
Ethanol	0.3	1.3
Isopropanol	0.2	0.16
Butanol	0.15	0.12