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Electrophoretic deposition of hydroxyapatite fiber reinforced hydroxyapatite matrix nanocomposite coatings

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ABSTRACT

Two-component suspensions of hydroxyapatite nanoparticles with spherical (S-HA) and fiber (F-HA) morphologies were prepared in isopropanol using triethanolamine (TEA) as the dispersant. In-situ kinetics of deposition and current density were recorded during EPD at 60 V from suspensions with different wt% of F-HA and TEA. *f* factor decreased against TEA concentration in all suspensions except the one-component suspension of F-HA particles. The detachment of particles from single component F-HA deposits did not occur during EPD due to the mechanical interlocking of F-HA particles in their microstructure. F-HA particles reinforced the coatings and prevented from their cracking during drying by bridging mechanism. S-HA particles infiltrated and filled the pores formed by stacking of the F-HA particles in deposit. S-HA particles were also grafted to F-HA particles in TEA-containing suspensions via hydrogen bonding between TEA molecules adsorbed on the particles. The coating deposited from the suspension with 75 wt% of F-HA particles had the best corrosion resistance in SBF solution at 37.5 °C.

1. Introduction

Hydroxyapatite (HA) is a calcium phosphate very similar to the inorganic part of the human bone and hard tissues both in morphology and composition [1]. HA has been widely used in biomedical applications due to its high bioactivity, biocompatibility, osteoconductivity and biodegradability [2–4]. However, HA has poor mechanical properties such as low hardness and fracture toughness restricting its usage in load bearing orthopedic applications [5–10]. To overcome this problem, HA is usually applied as the coating on the metallic implants such as titanium and 316 L stainless steel to combine the high mechanical strength of the underlay metallic substrate and excellent bioactivity of the upper HA coatings. HA coatings on metallic implants can also prevent from their corrosion induced by body fluid [11]. The corrosion of implant releases the metal ions into the surrounding tissues leading to their inflammation [12]. Moreover, in general metals do not have sufficient bioactivity and applying, for example, HA and bioactive glass coatings on their surface can significantly promote their bioactivity. Several processes have been used to apply HA coatings on the metallic substrates such as sol-gel [13,14], thermal [15] and plasma spraying [16], electrolytic deposition [17], electrodeposition [18] and so on. Electrophoretic deposition (EPD) is another technique which has been widely used in recent years to deposit HA coatings on the metallic substrates [19–30]. EPD is a two-step process: in the first step, charged particles dispersed in a suitable solvent move toward the oppositely charged electrode (substrate) under the influence of an applied electric field; in the second step, they deposit on the substrate and form a relatively dense particulate layer on it [31]. EPD has several advantages like simplicity, need to low-cost equipment, short formation times, forming the even coatings on the substrates with complex shapes and capability to control the microstructure and thickness of deposits by simple adjustment of EPD parameters such as voltage and time [32].

The kinetics of EPD can be stated by the following equation [32,33]:

$$\frac{dw}{dt} = f \cdot \mu \cdot \mathrm{E} \cdot \mathrm{c} \tag{1}$$

where $\frac{dw}{dt}$ is the EPD rate, μ is the electrophoretic mobility of particles, E is the applied electric field and c is the concentration of particles in the suspension. *f* factor or sticking parameter is a constant ($f \leq 1$) implying the efficiency of deposition [33,34].

Electrophoretic mobility of particles can be calculated by the following equation [35]:

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

where ε_0, ε_r, ξ and η are permittivity of vacuum, relative dielectric constant of suspension medium, zeta potential of particles and viscosity of suspension, respectively.

Another way to enhance the mechanical strength of HA is the addition of reinforcing second phase into its microstructure. Several

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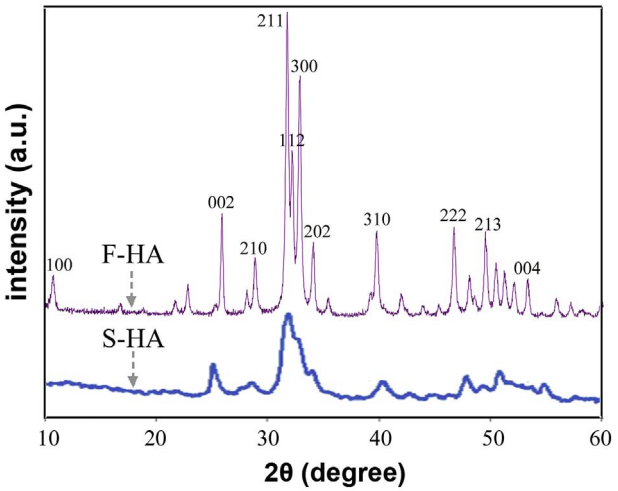

Fig. 1. XRD pattern for synthesized S-HA and F-HA powders.

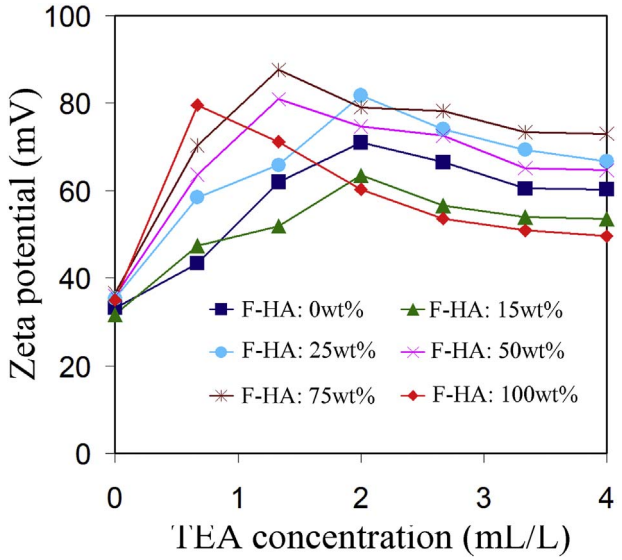

Fig. 3. Zeta potential of particles in the suspensions with different wt% of F-HA particles against TEA concentration.

reinforcing phase like Ti-Fe particles [36], rare earth oxides [37], alumina [38], zirconia [39] and carbon [40–42] fibers and carbon nanotubes [30,43–46] have been used to enhance the mechanical strength of HA. The reinforcing phase must also have high biocompatibility and bioactivity. So one-dimensional HA particles seem to be the most-promising reinforcement for HA. W. Suchanek et al. [47,48] fabricated HA/HA whiskers composites and found that HA whiskers increase the fracture toughness of HA without decreasing its biocompatibility and bioactivity. In this work HA particles with fiber morphology (F-HA) were used as the reinforcement to enhance the mechanical integrity of HA coatings. The effect of F-HA particles amount in the suspension on the EPD process as well as the characteristics of obtained coatings has been investigated in this work.

2. Experimental

Hydroxyapatite nanoparticles with spherical (S-HA) and fiber (F-HA) morphologies were synthesized according to the methods described in Ref. [49,50], respectively. X-Ray diffraction (XRD) analysis was used to identify phases in the synthesized nanopowders. The microstructure of nanopowders was also observed by the scanning electron microscope (SEM). Isopropanol (99.8%, Merck Co.) and triethanolamine (TEA, reagent grade, Merck Co.) were used as the solvent and dispersant for suspension preparation, respectively. To prepare the suspensions, firstly different concentrations of TEA (0, 0.67, 1.33, 2, 2.67, 3.33 and 4 mL/L) were dissolved in isopropanol by magnetic stirring for 15 min; then S-HA and F-HA particles with different wt% ratios (F-HA wt%: 0, 15, 25, 50, 75 and 100) but constant total particles concentration of 10 g/L were added into the prepared isopropanol-TEA solutions. The suspensions were then magnetically stirred and ultrasonically dispersed for 24 h and 10 min, respectively. The zeta potential of particles was measured in suspensions with different compositions by Malvern instrument. The samples for zeta potential analysis were prepared by the method described in Ref. [34]. Electrophoretic deposition (EPD) was carried out at 60 V using a two-electrode cell with an electrodes distance of 1 cm. The plates of 316 L stainless steel with the dimensions of 40 mm × 20 mm × 1 mm were used as the substrate. The substrate area of 20 mm × 20 mm was exposed to suspension during EPD; the reminder area of substrates was insulated by polymeric adhesive tape. The counter electrode was also a same plate as the substrate. In-situ kinetics of deposition and current density during EPD were recorded based on the method described in Ref. [34]. During in-situ recording of the EPD kinetics the voltage was applied for 6 min and then switched off for 2 min. The effective voltage (V_{eff}) across the suspensions was calculated by the following equation:

$$V_{eff} = V_{app} \cdot \left(\frac{i_t}{i_0} \right) \quad (3)$$

where V_{app} is the applied voltage (60 V), i_0 and i_t are the current density at starting point ($t = 0$ s) and moment t of EPD, respectively.

Sticking parameter (f factor) was calculated using the data obtained by in-situ recording of the EPD kinetics according to the Ref. [34].

The optimum concentrations of TEA in suspensions with different wt% of F-HA were determined by the results of zeta potential analysis.

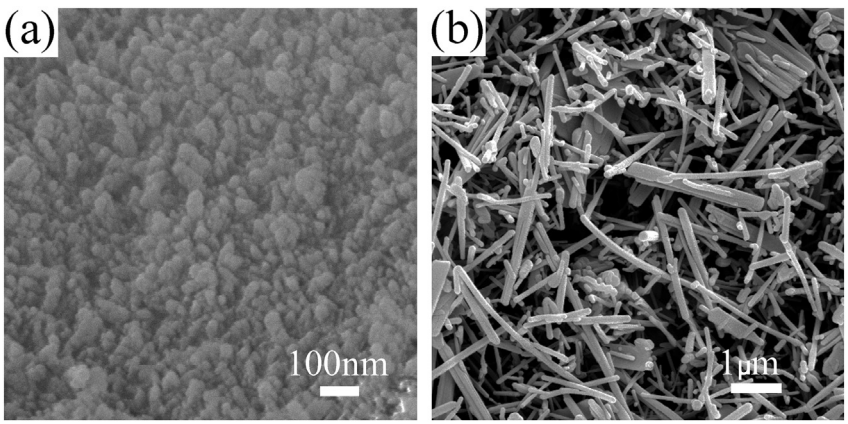

Fig. 2. SEM image for synthesized (a) S-HA and (b) F-HA nanoparticles.