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Structure, apatite inducing ability, and corrosion behavior of chitosan/halloysite nanotube coatings prepared by electrophoretic deposition on titanium substrate

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ABSTRACT

In this study chitosan/halloysite nanotube composite (CS/HNT) coatings were deposited by electrophoretic deposition (EPD) on titanium substrate. Using HNT particles were investigated as new substituents for carbon nanotubes (CNTs) in chitosan matrix coatings. The ability of chitosan as a stabilizing, charging, and blending agent for HNT particles was exploited. Furthermore, the effects of pH, electrophoretic bath, and sonicating duration were studied on the deposition of suspensions containing HNT particles. Microstructure properties of coatings showed uniform distribution of HNT particles in chitosan matrix to form smooth nanocomposite coatings. The zeta potential results revealed that at pH around 3 there is an isoelectric point for HNT and it would have cathodic and anionic states at pH values less and more than 3, respectively. Therefore, CS/HNT composite deposits were produced in the pH range of 2.5 to 3. The apatite inducing ability of chitosan-HNT composite coating assigned that HNT particles were biocompatible because they formed carbonated hydroxyapatite particles on CS/HNT coating in corrected simulated body fluid (C-SBF). Finally, electrochemical corrosion characterizations determined that corrosion resistance in CS/HNT coating has been improved compared to bare titanium substrate.

1. Introduction

Providing a desirable structure of an implant with a high surface compatibility between the implant and biological environment is one of the most important issues for biomaterial scientists [1]. They have been directed towards achieving this purpose by proposing many different types of biomaterials including polymers [2], ceramics [3], and composites [4–6] to deal with this challenge. Halloysite nanotube (HNT) is one of the well-known biomaterials that has been interested in bio-coatings and drug delivery systems. Although HNT has been proposed as a suitable candidate to replace carbon nanotube (CNT), there are few studies in this area [7,8]. HNTs have many properties that make them suitable for using as a surface coating for implants [9]. These properties can be improved further by combination with polymers. Co-deposition of HNTs with polymer eliminates the sinter process [10], improves delivery of active ions [11], creates superior adhesion, and enhances both the strength and toughness of the composite coating [12].

Chitosan (CS) is a natural and semi-crystalline polysaccharide which is biocompatible [13,14], biodegradable [15], antibacterial [16], capable of forming different shapes of films [17], antifungal [18], antioxidant [19], and mucoadhesive [20]. In a dilute acidic solution ($pH < 5.5$), chitosan has free cationic amino groups that enhance its activity.

Compared to other types of biopolymers, which have been normally used in tissue engineering, chitosan and its derivations have a broader range of applications including wound care [14], modification of implant surfaces [20–23], and antibacterial systems [15]. Also, chitosan is able to disperse and charge substances [24]. There are several strategies that have been developed to disperse nanotubes agglomerates in order to improve their performances and thus increase their applications [25].

HNT is an aluminosilicate nanotube that consists of Al_2O_3 and SiO_2 embedded in an outer tetrahedral layer and inner octahedral cylinder core, respectively [26]. Due to their useful properties including biocompatibility, biodegradability, non-toxicity, super dispersion, and sustained release rate [26–29], these materials have utilized for the fabrication of thin film biosensors [30], supercapacitors [31], biomedical implant materials and protective coatings [32,33].

Among the existing methods for the preparation of chitosan-based coatings [34–37], the electrophoretic deposition (EPD) technique has attracted greater interest due to its simplicity, ability to produce smooth coatings, and ability to deposit on complex shaped parts [38]. EPD is defined as a deposition of particles that have been electrophoresed in a suspension liquid (solvent) under an electric field (AC or DC) between two electrodes. In spite of the simplicity of this method, a great number of parameters can influence the deposition properties. These

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parameters can be categorized in two groups [38]: (i) those related to the suspension such as zeta potential, stability, and conductivity of suspension, and (ii) those related to the process such as the concentration of solids in the suspension and applied voltage. Zhitomirsky et al. [39] used HNTs to modify the surface of implants for the first time and developed composite, multilayer, and functionally graded chitosan–HNT–Hydroxyapatite films produced by EPD on platinum, stainless steel type 304, and platinized silicon. These composite films provided corrosion protection of stainless steel 316L substrates in simulated body fluid (ringer solution).

The goal of this study is to investigate the feasibility and properties of CS/HNTs composite films coated on a titanium substrate by EPD method. In this research, the effects of pH, parameters pertaining to the suspension, charging of HNTs, and CS/HNT deposit preparation on the microstructure, apatite inducing ability, and corrosion behavior of deposited films have been investigated.

2. Experimental procedure

2.1. Materials

Medium molecular weight chitosan (MW = 80 kDa) with a degree of deacetylation of about 85%, acetic acid (>98%), HNT with chemical formula $Al_2Si_2O_5(OH)_{4}.2H_2O$ and ethanol were purchased from Sigma-Aldrich.

2.2. Preparation of electrophoretic deposits

A medium molecular weight chitosan is used to prepare dilute chitosan solution by dissolving 0.5 g chitosan powder in 1 l of 1% acetic acid solution and stirring for 24 h at room temperature.

The baths used in electrophoretic process consist of a suspension of 0.6 g/l HNT with 30 vol.% pure water or 30 vol.% chitosan solution in ethanolic solvent. Compared to other types of baths, ethanol has advantages to decrease molecular hydrogen evolution. This is caused by water electrolysis and consequently suspension conduction [40]. The suspensions were ultrasonicated for 20 min after stirring by magnetic stirrer for 75 min in order to break down the agglomerates. Suspension pH was adjusted in the range of 2.6 to 3.6 by diluted hydrochloric acid. No additive was added as a charging and/or dispersion agent. To prevent ethanol evaporation and being contaminated, the electrophoretic cell was sealed with a paraffin foil.

Among the metallic implants, titanium has been broadly used for orthopedic prosthesis because of its low density, desirable corrosion resistance, and excellent mechanical properties [41]. Thus, commercially pure titanium and 316L stainless steel electrodes were used as a cathode and anode, respectively. The cathode to anode surface area ratio was selected equal to 10:1. This large ratio improves the distribution of electrical field and consequently the quality of deposit.

The surface of electrodes were polished by SiC abrasive papers and then rinsed with deionized water and ethanol in an ultrasonic bath. In case of titanium, the electrode was etched in a solution containing HF and HNO_3 for 10 s and rapidly rinsed in ethanol and dried.

Electrophoretic deposition was performed at 30 V DC power for 5 min at room temperature. A constant distance of 15 mm was chosen between electrodes. Two different coatings CS and CS/HNT were deposited. At least 5 samples were fabricated from each type. The deposited samples were dried and maintained in desiccator.

2.3. Characterization of deposits

The structure and morphology of coatings were studied by transmission electron microscopy (EM208, Philips) and scanning electron microscopy (JXA-840, JEOL). Energy-dispersive X-ray spectrometry (EDX, Oxford Instruments) was used for quantitative elemental analysis.

The crystalline structure of CS/HNT coatings was analyzed by X-ray diffraction (XRD, 3003 PTS, Seifert) with Cu-K_α radiation ($\lambda = 1.54$ Å) using the 2θ range of 10 to 80° with step size of 0.04° and a count rate of 50 s per step.

FT-IR spectroscopy (FT-IR, Nexus 870, Thermo-Nicolet) was used to depict intermolecular bindings between HNTs and chitosan in the wavenumber range of 4000–400 cm^{-1}. For this purpose the coating was removed from the substrate and mixed with potassium bromide.

The dispersion behavior of HNT particles was investigated by UV–visible spectroscopy (Capy 300 cone) in wavelength region of 250–800 nm.

Zeta potential and mobility of HNTs were also measured in different suspensions (Malvern, Sizer 3000 HsA).

The growth of carbonated hydroxyapatite assessments on coating w performed by immersion of CS and CS/HNT coated samples in corrected simulated body fluid (C-SBF) solution. C-SBF solution was prepared according to the procedure described by Kokubo et al. [42]. As it can be seen in Table 1, the composition of SBF is nearly equal to ionic composition of human blood plasma. The apatite inducing ability test was conducted by the incubation of samples in 50 ml C-SBF for 5 days at 36.5 ± 0.5 °C. After incubation, samples were taken out and rinsed with deionized water. They were subsequently dried in air and stored in a desiccator for further investigations. Carbonated hydroxyapatite deposition formed on the coatings was analyzed by SEM and FE-SEM/EDX.

Electrochemical corrosion behavior of uncoated and coated substrates was characterized by potentiodynamic polarization method (EG & G model 273 A). The counter and the reference electrodes were platinum plate and standard calomel electrode (SEC), respectively. The surface area of the working electrode was 1 cm^2. C-SBF at a temperature of 37 ± 0.1 °C was chosen as an electrolyte. Prior to polarization tests, the samples were immersed for 30 min in electrolyte to reach the steady state condition. The potential was scanned from −300 mV to +500 mV versus open circuit potential at a rate of 1 mV/s. The corrosion potential (E_{corr}) and corrosion current density (i_{corr}) were extracted by Tafel extrapolation method from polarization curves.

3. Results and discussion

3.1. Suspensions properties

3.1.1. Zeta potential and mobility

Fig. 1 shows zeta potential and mobility of HNTs in different suspensions. It is obvious that pure water and ethanol with 0.5 g/l chitosan solution provide the lowest and the highest zeta potential and mobility, respectively.

It can be seen that the aqueous bath provides lower zeta potential and mobility for HNTs compared to alcohol-based bath. Due to the superior liquid/solid interface energy of aqueous medium, which is shown by inferior zeta potential, dispersion of nanotubes in water would not be desirable. On the other hand, alcoholic medium provides more zeta potential, lower viscosity, and therefore a suitable mobility for HNTs.

Table 1
Composition of the corrected simulated body fluid (C-SBF) that was used for in vitro bioactivity assessments and ionic composition of human blood plasma [42].

Ion	Ion concentration (mM)	
	Blood plasma	SBF
Na^+	142.0	142.0
K^+	5	5.0
Mg^{2+}	1.5	1.5
Ca^{2+}	2.5	2.5
Cl-	103.0	147.8
$HC\mathbf{O}_3^-$	27.0	4.2
$HP\mathbf{O}_4^{2-}$	1.0	1.0
$S\mathbf{O}_4^{2-}$	0.5	0.5
pH	7.2–7.4	7.40