

STUDY ON THE DEGRADATION BEHAVIOR NANOCOMPOSITES COATED ON MAGNESIUM ALLOY FOR BONE IMPLANTS

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Abstract

Magnesium and its alloys as biodegradable implant materials provide both biocompatibility and suitable mechanical properties compared to human cortical bone. However, the high degradation rate of magnesium alloy in physiological environments hinders their uses in hard tissue engineering. This paper investigates porous bioactive nanocomposites film coating on magnesium alloy AM50 which were prepared by dip coating method. The deposited porous layers were prepared from synthesized Hydroxyapatite nanoparticles (n-HAp) and Poly (ϵ -caprolactone)(PCL) solution. The micro-porous size of the membrane layer coatings on Mg is relatively uniform distribution and can be controlled during the manufacturing process. The biocorrosion behavior was investigated by electrochemical polarization test. The results manifested that, the corrosion resistance of coated samples were improved significantly particularly after doped n-HAp into PCL membranes compared to untreated sample. Moreover, Immersion tests demonstrated that the nanocomposites layer could protect magnesium alloy from high degradation rate. As a result, the bioactive layer motivated the precipitation of apatite-like in simulated body fluid (SBF) at 37 °C in a short time. In addition, the mechanical integrity of treated samples showed higher resistance upon degradation process. Collectively, the polymer bioactive nanocomposites membrane layer may be potentially applied in the future for orthopedic application.

1. Introduction

Magnesium is a remarkable material, whose outstanding properties make it the material of choice for many applications in the automotive, aircraft, aerospace, architectural, packaging industry and biomedical. However, Magnesium and its alloys are susceptible to dissolution in aqueous environment; especially in those containing chloride ion electrolytes, mainly due to they have very low corrosion potential [1]. Nevertheless, Biodegradability of the magnesium is preferable

advantage compared [2, 3] with the conventional implants which are well known non-degradable materials such as Cobalt-chromium based alloys, titanium and its alloys and stainless steels [4-6]. Implant ability to be degraded after the bone has healed is a much desired characteristic as problems may arise if the implants are not degradable [7]. Based on this consideration a more encouraging is needed to control the degradation rate and improve the corrosion resistance of magnesium which imposes a limitation for their widely use in orthopedic and cardiovascular applications.

In this sense, a great deal of effort has been done to improve the general corrosion resistance of magnesium based alloys, such as decreasing impurity level [8], adding superior corrosion resistance materials and producing a more homogeneous microstructure [1]. However, surface modification can be considered as an ideal way to improve the biological functions, control the degradation rate, avoid severe localized corrosion on magnesium surface and improves the mechanical interlocking between the implant and the bones, particularly organic coatings. Organic coatings can act as a barrier layer to separate the substrate metal from its environment at the first healing period. Different studies have been investigated pure polymeric coatings magnesium based alloys, such as lately. et.al [9], Li. et.al [10], etc. but to date, their results are not conclusive where they cannot meet the biological functions requirements. In some cases, the presence of corrosion inhibiting in the coatings can further significantly their protection performance as well as biological functions.

The coatings layer should be osteoconductive so that osteoprogenitor cells can adhere and migrate on the scaffolds, differentiate, and finally form new bone after fully degradation of the 3-D temporary layer. Nanohydroxyapatite (n-HAp) is considered as an ideal bioactive material whose composition and crystal structure is very similar to that of bone [7, 11], and has bone bonding ability *in vivo* condition. In addition, because of its excellent osteoconductivity, osteoinductivity, abrasion and corrosion resistance and high chemical stability, has been devoted in many of forms such as substitute and regeneration material. However, regarding all of these advantages, hydroxyapatite has very poor mechanical stability, inherent brittleness and difficulty for processing contracts its uses for the regeneration of load-bearing bone defects [11]. Because ideal coatings on magnesium surface have to serve as a platform for biological functions, such as cell affinity, osteoconductivity and enhanced bone formation, behind the corrosion protection, hence synthesized polymeric/inorganic nanocomposites seem as a smart way to play this role. These properties of both hydroxyapatite as nano fillers and PCL based nano composites film coating magnesium can be combined to form multifunctional nanocomposites.

Collectively, it is thus necessary to develop coatings which incorporate nHAp reinforced polymers via reliable method that can be easily used to control the degradation rates and layer thickness and modify the biological functions of magnesium surface. The objective of the present study was to demonstrate dipped magnesium samples into PCL/nHAp to introduce new nanocomposites porous structure film with a border range of properties. Alternative properties of these composites coating magnesium substrates may provide routes to new biomaterials with

useful corrosion protection and biological properties. The pore structure, pore distribution, biocorrosion properties and bioactivity of the coatings layer on magnesium surface were systematically investigated.

2. Experimental section

2.1. Sample preparation

Die casting magnesium alloy AM50 was chosen as a substrate material and mainly to validate degradation rate and corrosion behavior at under test condition. AM50 was cut into square specimens with dimensions of 12 x12 mm² and 2 mm in thickness. Prior to coatings process, the samples mechanically polished with 600-1200 grit waterproof adhesive paper and then polished with 1 μm diamond grinding. Thereafter the samples were cleaned ultrasonically in acetone for 5 min to remove residual grease and distilled water and dried.

2.2 Preparation and coating procedure of hybrid nanocomposites PCL/nHAp layer

The deposited porous layers were prepared according to the following process: two PCL (Sigma Aldrich, average molecular weight, Mn ranged from 70,000 to 90,000 by GPC) solutions (6 wt %) were prepared by dissolving polymer granules in dichloromethane (DCM) solvent. Colloids were prepared by mixing the synthesized HAp nanoparticles, as shown in Fig.1 (further information about synthesized HAp nano-scale can be found in our previous publication [12]) with the obtained PCL solutions and stirred continuously for more than 24 h followed. Two suspensions solution were prepared using one concentrations of n-HAp (10 and 25 wt %) with every PCL concentration. In total, four different formulations (1 pristine PCL solutions and 2 colloids) were prepared and investigated as coating layers on Mg-alloy substrate. The prepared substrates were immersed into the solution for 25 s to allow the wetting. In order to obtain a stain-free surface, the specimens were slowly pulled out of the solution with a speed rate around of 2 mm/s. Post dip-coatings all the specimen were introduced to a hot plate at 160 °C for 10 min to remove the moisture and entrapped air from the substrate surface. All the coated samples were introduced to vacuum drier (10 mbar).

2.3. Characterization

The surface properties of the deposited layers were characterized using JEOL JSM 820 scanning electron microscope coupled with energy dispersive spectrometer (EDS). These images were processed and analyzed with imageJ software (National Institute of Mental Health, Bethesda, Maryland, USA.) to extract information about mean pore length, porosity and uniformity of the coated layers. Prior to imageJ processing, the scale was set to the scale bar recorded in the image to obtain lengths in micrometers instead of pixels.

2.4. Electrochemical corrosion test

Prior to polarization test, the samples were immersed in 1000 ml SBF for 20 min to establish a relatively stable open circuit potential. The electrochemical behavior of both the uncoated and coated samples which were conducted in standard simulated body fluids (SBF) at a PH 7.4 were

investigated potentiodynamic polarization test (263A, EG&G PAR, USA)). A three-electrode cell with the sample as the working, Ag/AgCl/1 M KCl (Satd.) as the reference, and platinum as the counter electrode were used. The exposed area of the working electrode (controller and deposited layer samples) to the solution was 1 cm². A 1 mVs⁻¹ scanning rate was applied during the potentiodynamic polarization test. The changes in the free corrosion potential (E_{corr}) were monitored as a function of time. The temperature was controlled to 37 ±0.5 °C during the test. The corrosion test of the samples was calculated by extrapolating the polarization curve according to ASTM-G102-89.

2.5. Immersion tests

Immersion test was performed in a standard simulation body fluid (Hank's balanced salts, H2387, Sigma Aldrich, Korea), the specimens for each condition were immersed in 100 ml of solution. The electrolyte was saturated with atmospheric oxygen and doesn't stir during the experiments. The temperature was controlled to 37.5 ±0.2 °C during the test. The immersed samples were extruded; gently rinsed with distilled water and dried at room temperature to avoid cracking. The surface appearance of the coated and uncoated immersed samples before removing the residual coatings and corrosion products were observed by SEM.

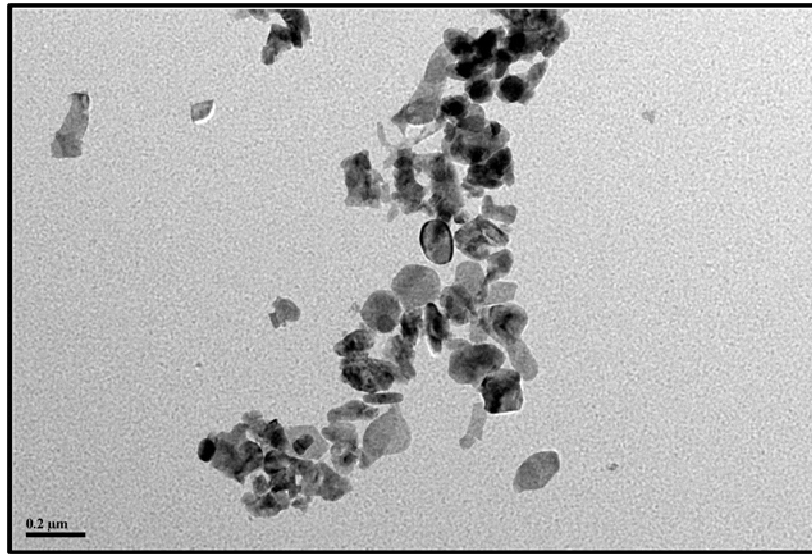


Fig.1. TEM morphology of synthesized HAp nano-scale

3. Results and discussion

3.1. Surface properties of the coated samples

Fig.2 typically shows the surface morphology in SEM of the coated magnesium samples with plain PCL membrane layer and PCL/n-Hap composites layer at the pre-mentioned concentrations. It is clear that the plain PCL coated samples showed fairly full network structure in a porous size ranged from 3 to 8 μm. furthermore, with incorporation nHap into PCL membranes layer the porous structure went to decrease with increasing the hydroxyapatite content in the prepared layers, where, at 25 wt% Hap the porous

almost closed with Hap particles as shown in Fig.2c. However, in comparison with low content of Hap the particles inside the matrix introduced a good adhesion within the polymer matrix.

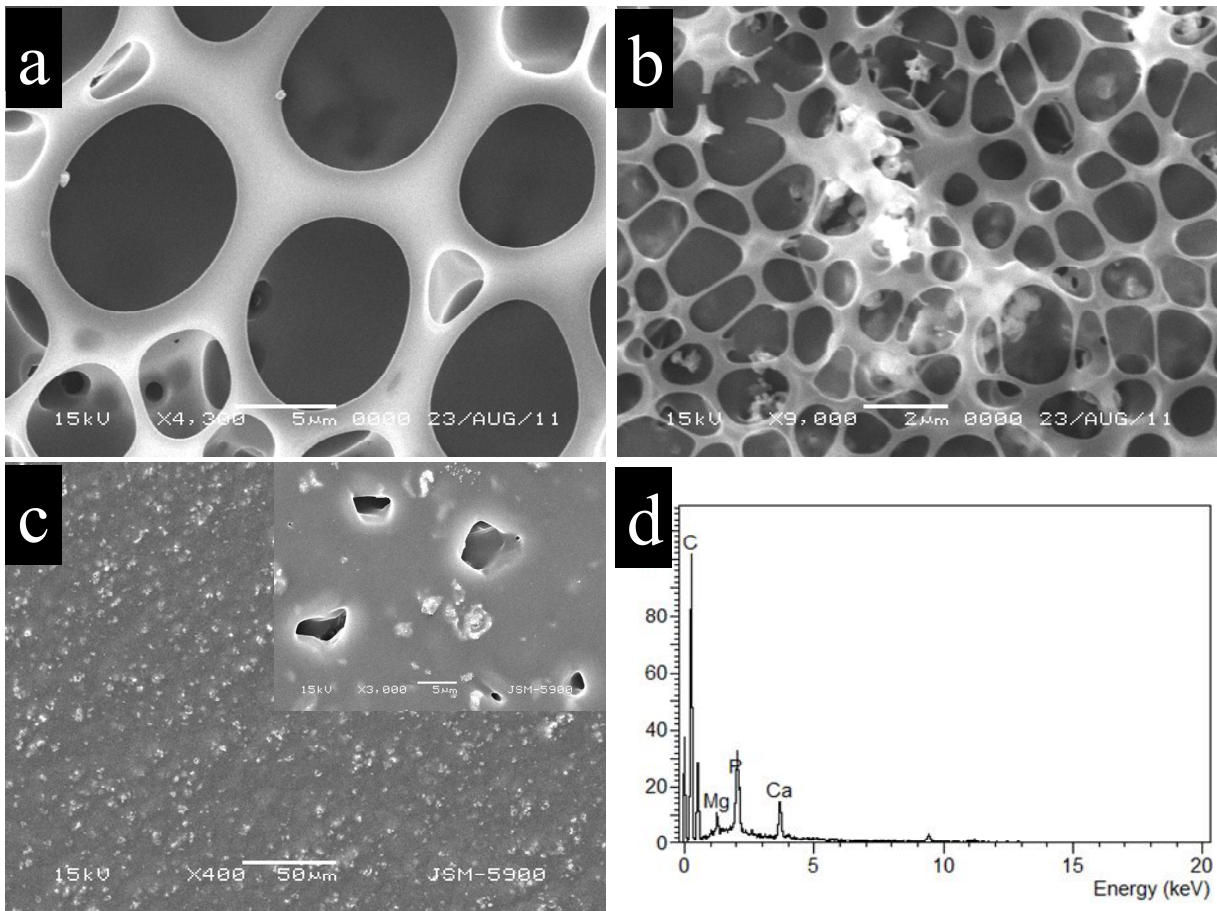


Fig.2. Surface appearance in SEM of magnesium coated samples with plain PCL (a) and (b) nHAp at 5 and 10 wt %, PCL (c) and (d); SEM-EDX of the composite coated samples. Insets are their water contact angle

3.2. Electrochemical corrosion analysis

Representative potentiodynamic polarization curves obtained from the un-coated and coated AZ31 magnesium samples in SBF at 37 °C are displayed in Fig.3. It is noticed from the E_{corr} that the polymer composite-coated magnesium alloys slowly shifted the open circuit potential to a positive potential. At the same time, the values of the corrosion current (I_{corr}) of the polymer composite-treated samples, especially 25 wt% sample, significantly decreased as compared with those of the uncoated sample. This reason refers to the HAp nanoparticles relatively closed the microporous and decreased the potential surface corrosion area then reduced the corrosion rate. In addition, Hydroxyapatite (HAp) is expected to show high corrosion resistance because the thermodynamic stability of the HAp structure is remarkably high. We can show that the corrosion potentials in the composite coatings were noble than uncoated magnesium bar, being -1.146 V and -1.187 V in 10 and 25 wt % HAp coating respectively. Actually, the AZ31 corrosion potential has lower value than as measured during this study, it was reported in

different literature around of -1.67 V in sodium chloride solution (free potential) [12]. This is due to two reasons. The first reason, the formation of the hydroxide layer during the immersion test before introduces to the polarization test (in this study the exposed time was 30 min). The second reason, it may be the low impurities level in the prepared alloy. As a result, both the E_{corr} and I_{corr} showed that the PLA membranes deposited samples were able to enhance the corrosion resistance of magnesium alloy, thereby suggesting a much lower corrosion rate on the coated alloy compared to that on the un-coated specimen.

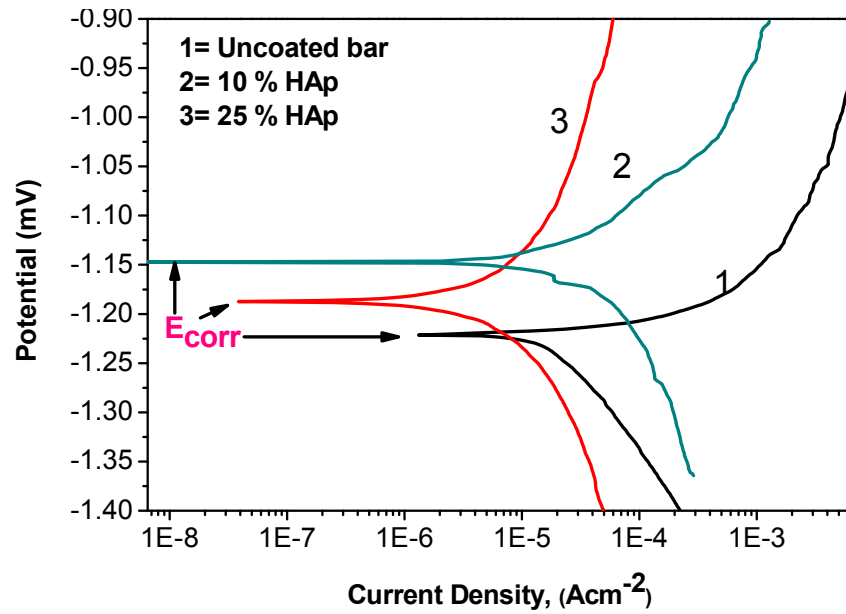


Fig.3. Potentiodynamic polarization curves for coated and uncoated samples

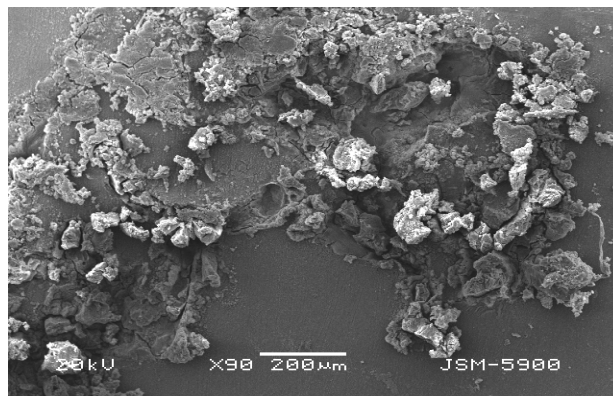


Fig.4. Surface appearance in SEM after immersion in SBF for 15-day uncoated samples

3.3. Immersion tests

Fig.4 typically shows the selected SEM images for the uncoated samples after immersion in SBF at 37 °C for 20 day and before removing the corrosion products. It is clear from these images that the uncoated samples showed cleavage and much attack by water molecules. It needs to be mentioned that the water diffusion through tiny micro or nano defects on the coating layer would be able to deteriorate the coatings and lose the adhesion of the organic layer on the substrate. Reports [13] have indicated that when the water molecules come to contact with magnesium surface by the electrochemical reaction hydrogen gas will evaluate. However the porous layer for pure polymer fabricated via dip-coating cannot provide fully porous structure mainly due to the organic layer contains from three films primer, intermediate and top-coating film. The primary film is responsible to provide a good adhesion between the whole organic layer and metal substrate. Hence, the primary film is complete dense-non porous phase structure. In that case the hydrogen evaluation will be damp under this film, with increasing the pressure back diffusion the tiny micro contains in the primer film not sufficient to provide the vast speed of hydrogen release from magnesium substrates with further incubation time. While the composite coatings may contain fully porous, this establishes between nano-particles and polymer matrix, sufficient to allow evaluation of hydrogen gas easily via the polymer matrix layer. To inform our hypothesis, the composite coating layer is still in a contact and resists the blasting or/and delamination from the substrates, Fig.4a. From this point of view, it is deduced that the incorporation of nHAp into the polymer matrix could provide a sufficient stability of the coatings layer on magnesium substrates.

4. Conclusion

The present study has investigated new advanced composite coatings film on magnesium substrates developed using dip-coating technique. Furthermore, the evaluation of these coating films under in vitro simulated physiological conditions was dramatically studied. In fact, the surface properties of current bone implants have to be modified in a way to better mimic the surface characteristics of bone. In general, the results obtained in this study indicated that the incorporation of nHap into the polymer matrix layer modified both the degradation performance and biological functions of magnesium substrates and induced interesting changes in the magnesium surface properties such as, chemical composition of the treated surface, surface roughness and watability. Further research will be needed to evaluate the degradation performance and biological functions of hybrid polymer matrix nanocomposites coated on magnesium based implants, using an in vivo animal model.

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