EXAMINATION OF COATING PARAMETERS OF BIOPOLYMER COATING ON AZ91D MAGNESIUM ALLOY USED AS IMPLANT IN HUMAN

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Abstract

In the last decade, magnesium alloys were studied as biodegradable metallic materials due to their unique mechanical properties, such as density, specific strength and modulus of elasticity similar to human bone. However, they extremely susceptible to corrosion in physiological environment and this situation hinders their possible implementations in medical applications. This research investigates the effect of Poly (vinyl alcohol) (PVA) coating on the in-vitro corrosion behavior of AZ91D magnesium alloy. The coating was achieved by dip coating method in different polymer concentrations and immersion cycles. The coating morphology was examined by scanning electron microscope (SEM) equipped with an energy dispersive spectrometer (EDS). The degradation rate of AZ91D alloy was determined by weight loss experiments in simulated body fluid (SBF). Results have shown that the biopolymer coated specimens have better degradation resistance than uncoated AZ91D alloys, which could be used in load bearing orthopedic applications in the very near future.

Keywords: Magnesium, AZ91D, PVA, coating, simulated body fluid (SBF)

1. INTRODUCTION

Accident rates increase every year and bone fractures are one of the dreadful consequences of these accidents. Significant percentage of these fractures are too complex that, they need surgical bone implants. Consequently, novel and safer materials ought to be researched as potential biomaterials. In recent years research of magnesium and its alloys has started for different kind of applications. These studies were not only about aerospace, electronics or automotive applications but were also in biomedical fields. There are several significant advantages of magnesium and its alloys such as low density, high specific strength and good castability. They also show tensile strength, with a yield strength and Young's modulus similar to that of natural bone, which allow these alloys to be considerable for orthopedic applications [1, 2]. Aside from other conventional metallic biomaterials, biodegradability is another advantage of magnesium based biomaterials. At this point, the definition of biodegradable metals will help us to understand their importance at biomedical applications. Biodegradable materials are metals expected to corrode gradually in vivo, with an appropriate host response elicited by released corrosion products, then dissolve completely upon fulfilling the mission to assist with tissue healing with no implant residues [3]. Complete dissolve of biodegradable metals after tissue healing saves both the surgeons and the patients from another operations. It is known for a fact that magnesium ions are cofactor for many enzymatic reactions which makes them essential for human physiology. The recommended daily intake for adults of magnesium is 240–420 mg day^{-1}. These properties of magnesium make it harmless for human body after the in-vivo degradation [4, 5]. However fast in-vivo corrosion rate of magnesium and its alloys hinder their applications as biomedical materials. When the magnesium alloys are used for fixing the damaged bone tissue, they usually lose their mechanical integrity before the healing process is completed [6]. This drawback creates a massive challenge for scientists and engineers. Addition of high purity alloys and rare earth elements are convenient methods to cope this challenge.

Although general corrosion of magnesium alloys can be controlled, these methods are not suitable for controlling the internal and galvanic corrosion. This problem can be eliminated by coating of magnesium alloys

which is one of the most effective methods [7, 8]. Coating methods can be classified basically into two classes: conversion and deposited coatings. Conversion coatings depend on specific reactions between the base material and the environment. Typically during these reactions, substrate surfaces are converted into an oxide layer by chemical or electrochemical processes. The produced layers show ceramic like character. Deposited coatings consist mostly of organic materials and can be obtained by many different methods e.g. spraying, dip coating, spin coating. The common expected outcomes of these coating methods are enhancement of corrosion resistance, biocompatibility and osteointegration [9].

In this study AZ91D samples were coated with PVA Poly (Vinyl Alcohol) by simple dip coating method to reduce their degradation rate. PVA (and PLGA copolymers) is among the few approved synthetic polymers for human clinical applications due to their excellent biocompatibility. They are also biodegradable through a simple hydrolysis of the ester bonds into lactic and glycolic acid, which are excreted by normal metabolic pathways [5]. PVA which is also the polymeric material used for designing new coatings, is water soluble, biocompatible and has excellent physical properties [10]. After the coating procedure the coating morphology and the impact of coating on the corrosion rate change were examined. Weight loss evaluation were conducted to determine the degradation rate. The results were compared in order to determine most convenient polymer concentration and immersion cycle for each coating polymer.

2. MATERIALS AND METHODS

2.1 Sample Preparation and Coating Procedures

Die casting magnesium alloy AZ91D was chosen as the substrate material due to its precise chemical composition. AZ91D specimens were provided by a local foundry. The specimens were cut with METKON MICRACUT 150 PRECISION CUTTER (Turkey) and polished with 220 grit SiC abrasive paper. Degreasing process was accomplished by acetone in an ultrasonic bath and specimens were rinsed with ethanol after degreasing then specimens were dried in ambient air.

PVA Poly (Vinyl Alcohol) was purchased from Sigma – Aldrich. The average molecular weight of PVA were 31000 – 50000 Dalton. Deionized water used as a solvent. PVA powders were solved in deionized water with %4wt concentration under constant temperature at 90°C and magnetic stirring for 1 hour.

The process was carried out with a custom-made dip coater from 3G Project Design (Turkey) depicted in Figure 1. The sliced specimens were dipped for 5, 7 and 10 s and withdrawn at the speed of 1 cm/min 100 times. After coating procedure, coated specimens were hanged in oven vertically at 115°C for 14 h.

Figure 1 Custom made dip coater

2.2 Coating characterization

The surface properties of the coated layers were examined with JEOL SEM 5410LV operated at 20 kV. The images were taken at x35, x500, and x1000 magnifications for each coated specimen and an uncoated specimen.

2.3 Immersion Tests

The immersion tests were conducted in SBF (simulated body fluid) which was prepared according to Tas method [11]. Each specimen was immersed in 100 ml SBF separately. The degradation rate was measured by evaluating the total weight loss from the specimens for 12 and 24h.

3. RESULTS AND DISCUSSION

Die cast AZ91D specimens were cast into permanent mold and not heat treated after casting. Chemical composition of AZ91D specimens was given in Table 1.

Table 1 Chemical composition of AZ91D test pieces.

	Al	Zn	Mn	Si	Cu	Ni	other	Mg
Nominal, wt.%	8.1-9.3	0.4-1	Min 0.13	Max 0.30	Max 0.01	Max 0.001	Max 0.3	Balance
Measured, wt.%	9.10	0.70	0.25	0.09	0.01	0.003	0.22	balance

Initial characterization of test pieces was given in Table 2.

Table 2 Initial characteristics of AZ91D test pieces.

Property	Sample 1	Sample 2	Sample 3
Weight (g)	1.2034	1.0003	0.7744
Surface Area (cm^2)	3.27	2.80	2.80
Chemical Composition	AZ91D	AZ91D	AZ91D

Test pieces were then coated according to the parameters given in 2.1. Properties have changed as in the Table 3 after coating and immersion in simulated body fluid (SBF). In order to remove the chloride and hydrate reaction products from surface, test pieces were rinsed in chromic acid before weighting.

Table 3 Mass loss of AZ91D test pieces.

	Property	Sample 1	Sample 2	Sample 3
Weight (g)	After Coating	1.2309	1.0318	0.7993
	PVA Deposited	0.0275	0.0315	0.0249
	After 12h Immersion	1.2142	1.0120	0.7880
	After 24h Immersion	1.2140	1.0111	0.7880
Mass Loss (%)	After 12h Immersion	1.357	1.920	1.412
	After 24h Immersion	1.373	2.006	1.412

The weight loss was measured after each experiment and the corrosion rate (r) was calculated in $mg.cm^{-2}.day^{-1}$ according to Equation 1.

$$r = [(w-w_i) \times 1000] / (A \times t) \quad (1)$$

Where;

r: corrosion rate ($mg.cm^{-2}.day^{-1}$)

w_i: initial weight before immersion (g)

w: weight of specimen after immersion (g)

A: surface area of specimen (cm^2)

t: duration of immersion (day)

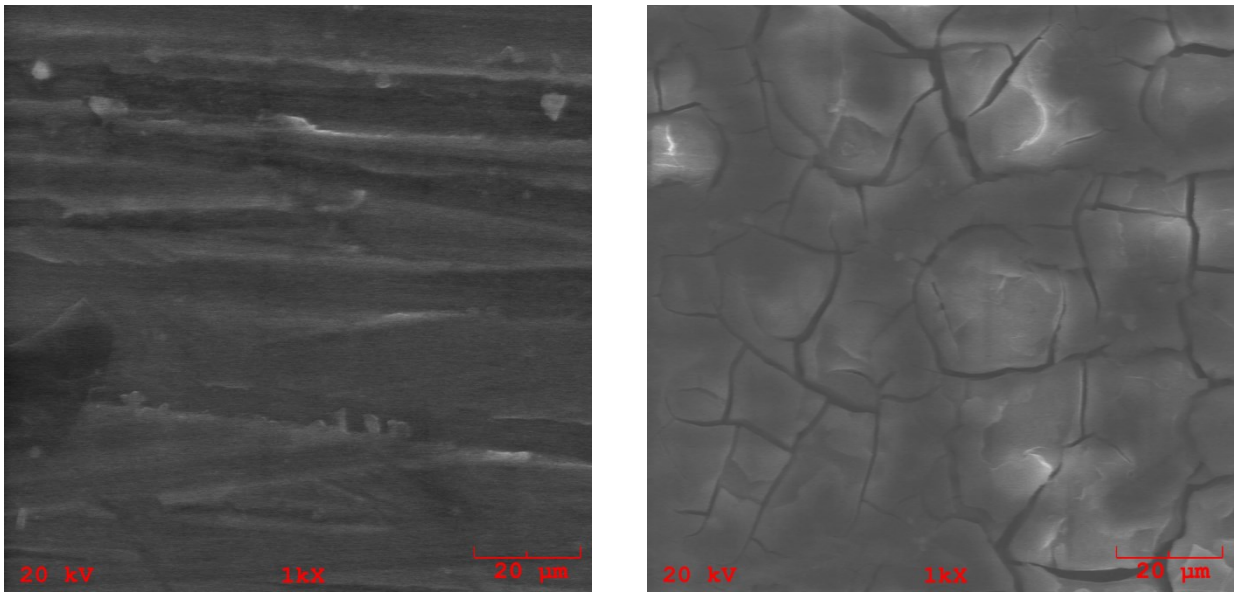
Corrosion rate of each specimen was given in Table 4.

Table 4 Corrosion rates of specimens coated with different parameters

	Sample 1	Sample 2	Sample 3
Corrosion Rate ($mg.cm^{-2}.day^{-1}$)	15.750	15.714	12.357

The results have shown that PVA coating on magnesium alloy is only effective on the reduction of corrosion rate after a critical coating thickness. The best result was achieved on the specimen which was immersed for 10 sec in each cycle during dip coating.

SEM micrographs of specimens before and after immersion in SBF were provided in Figure 2a and Figure 2b.



(a) (b)

Figure 2 SEM micrographs test pieces; a) uncoated, b) PVA coated

CONCLUSIONS

The rapid corrosion tendency of magnesium alloys are the main problem in the production of implants. This rapid corrosion behavior results in formation of excessive amount of Mg^{2+} ions and early failure of implant before healing process is complete.

Although test results have shown that the coating process obviously enhances the corrosion resistance of AZ91D, the thickness of coating must be over a critical value to provide this resistance. Further investigations will reveal the optimal coating parameters for promising magnesium alloys.

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