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Chitosan/Hydroxyapatite coating of AZ91 Magnesium Alloy by using Electrophoretic Deposition

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Abstract. Due to their good properties, including biodegradability and similar characteristics to natural bone, magnesium alloys have potential applications in implant manufacturing for biomedicine and orthopedics.In this study, chitosan or/and hydroxyapatite layers were performed on the surface of AZ91 magnesium alloy using electrophoretic deposition process. The surface microstructure of coating, mechanical properties, hydrogen evolution, pH and wettability were characterized with different techniques including scanning electron microscopy, vickers microhardness, immersion test and contact angle test. The results showed that, the coating layers were obtained can improve the corrosion resistance, mechanical properties, wettability making AZ91 a promising material to be used as a biodegradable alloy for biomedical applications.

1 Introduction

Due to its high strength, good corrosion resistance, and superior castability, AZ91 magnesium alloy is the most widely used type of cast magnesium alloy. Due to its non-toxicity and outstanding mechanical properties, AZ91 magnesium alloy becomes a desirable candidate. Since AZ91 magnesium alloys have rapid corrosion rate under physiological conditions, their actual clinical applications have been constrained. Therefore, one of the important difficulties to address for the creation of biodegradable implants is enhancing the corrosion resistance of the AZ91 Mg alloy [1].

One of the coating surface technique is electrophoretic, which is used to increase the corrosion resistance of conductive materials like magnesium. When compared to other coating techniques, electrophoretic coating has a number of advantages, including uniformity, low porosity, coating of complex geometry, excellent efficiency, inexpensive for mass production, and environmentally friendly nature [2].

As a natural of biopolymer that used for tissue engineering, chitosan (CS) is the most promising options. This polymer exhibits a special combination of features, including antibacterial activity, chemical stability, biocompatibility, and effective film forming properties [3].

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Hydroxyapatite (HA) is a bioceramic material used for soft tissue repairs, bone fillers, bone tissue engineering scaffolds, bone loading, and bioactive coatings due to their superior biocompatibility, osteoconductive characteristics, and similarity to the inorganic component of human bones[4,5].

The aim of this study is to investigate a composite coating of chitosan or/and hydroxyapatite on AZ91 magnesuim alloy as a substrate by EPD to improve the hydrophilic properties and corrosion behavior of an alloy.

2 Experimental works

2.1 Substrate Specimen

A plate of AZ91 magnesium alloy with composition listed in Table 1 has been cut by wire cutting machine for cylindrical samples with dimensions (10*5) mm were utilized as deposition substrate. The Mg specimens polished with (SiC) papers (180 to 2500 grits), and then washed in acetone, and dried with hot air.

Table 1. Chemical Compositions of AZ91Alloy.

Elements	Mg	Al	Zn	Mn	Si	Cu
Wt.%	89.512	9.079	1.151	0.107	0.135	0.016

The microstructure of AZ91 was examined using optical microscopy by using (280 XEQ-MM300 TUSB). Non-equiaxed and fine grains of the plate can be observed in the image of an optical microscope in Figure 1.

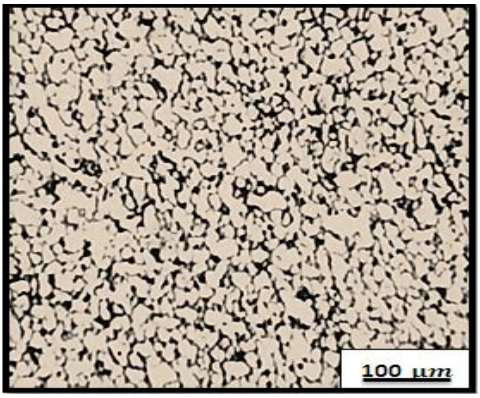


Fig. 1. Optical Micrograph of AZ91 Mg Alloy

2.2 Preparation of Coating

Coating solutions were prepared by dissolve 0.5 g/ L of chitosan (MW=300 kDa, Across, with around 85% deacetylation), in acetic acid solvent at room temperature and stirring for five hours. Deposition was performed by using the suspensions of 0.5 g/L chitosan without and with HA powders (1.5, 10 and 15 g/L), in the mixture of (95 vol.% methanol_5 vol.% water) containing 0.05 vol.% acetic acid (enhance dissolving of chitosan). The magnetic stirring of suspensions took place during a 24-hour period and ultrasonication (Bandelin, Sonopuls HD 3200, 20 kHz) for 30 minute to break down the agglomerates.

2.3 Electrophoretic Deposition (EPD)

In electrophoretic deposition 316L SS was used as an anode and AZ91 magnesium alloy as a cathode. The cathodic and anodic electrodes were cleaned in ethanol and dried prior to deposition. After that, they immersing in a 150 ml of beaker filled with coating solution. In the EPD cell, the electrode spacing was kept at 1 cm. The EPD technique was carried out in a glass beaker, during the whole period of process, the magnetic stirring was used to ensure the properly dispersed of particles.

After preparing the suspensions by adding different weight ratios of powders and the binder to alcohol and determining the optimum conditions. The PH of the solution was reduced to (4_5) before coating by the addition of HNO3 acid, voltage and time deposition were (20 V and 3 min.) to achieve a uniform coating layer and free of segregation or agglomeration. After that, the coated samples were carefully taken out of the EPD cell and allowed it to dry for 24 hours at room temperature. Table 2 shows the symbol code and description of various AZ91 specimens (with and without coating).

Table 2. The AZ91 Specimens With and Without Coating

Sample Code	Chitosan(g/L)	HAP (g/L)
S0	-	-
S1	0.5	-
S2	0.5	1
S3	0.5	5
S4	0.5	10
S5	0.5	15

3 Characterization of the Coating

Several tests, such as SEM, vickers hardness (HV), hydrogen evolution, pH measurement and contact angle (CA) must be performed in order to demonstrate the characterization of polymer coatings with and without HA particles. The surface morphology of the coated specimens was examined by using a MIRA 3-XMU scanning electron microscope (SEM). Vickers micro hardness testing machine with a load of 50 gf (gram force) and a dwell time of 10 second was used to measure the mechanical property of the coating. Both coated and uncoated AZ91 magnesium samples conducted hydrogen evolution testing. The samples were dipped in the coating solution and avoided to make contact with any surfaces.

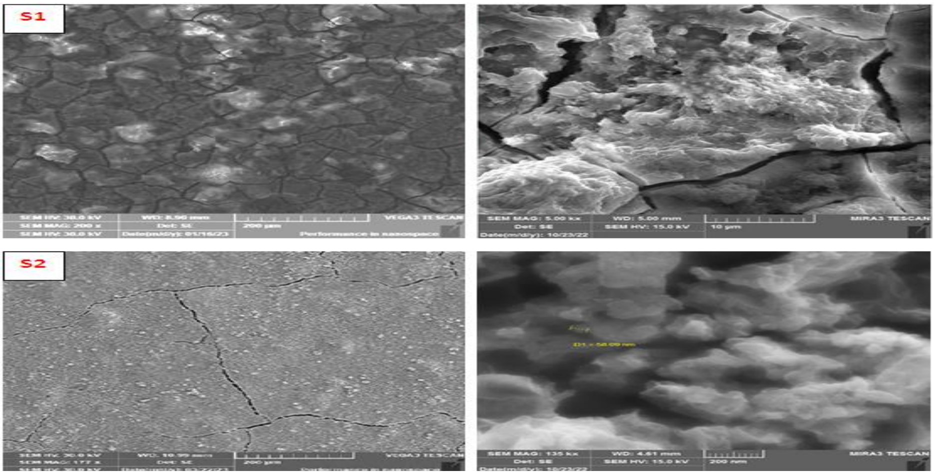
The amount of hydrogen (H_2) evolution can be used to as an indicate to corrosion behavior of the coating. Specimens were immersed in ringer solution as electrolyte medium at 37°C ± 1 for 7 days to obtain the hydrogen evolution and 24 hours pH measurements. A pH device of the "Hannaii type" was used to determine the pH of the solution.

The pH of the solution was considered as an indication of the coating's corrosion resistance. Using a contact angle device "Powreach, ST200KS, China" to measure the wettability of specimens.

4 Results and discussions

4.1 Morphological characterization

Figure 2 shows the results of SEM for CS and CS with HA composite coating for different weight ratio of HA. By examining 2D images of the coated surfaces, it can be shown that the specimens have some differences of surface topography.The surface morphology of coating for EPD method on AZ91 magnesium alloy as shown in FE-SEM photos. In order to produce coatings with the proper amount of content, the EPD coating on the surface morphology of AZ91 substrate was examined. The FESEM results of the CS and CS with HA composite coating for various weight ratios and magnifications are shown in Figure 2. By looking at 2D images of the coated surface, it can be seen that the specimens have quite different surface topographies. In general, the hydroxyapatite is indicated by the bright areas in the FE-SEM pictures, whereas the chitosan phase is shown by the dark areas. The development of fractures during the coating's drying process is one of the key problems with the electrophoretic approach. The main reason of crack development at the coating is a thermal expansion mismatch between the coating (CS and HA) and the magnesium-based alloy substrate [6]. Additionally, it can be caused by the chitosan polymer shrinking when the solvent evaporates. The coated sample with only CS have a large cracks and appear to be joined together, whereas in composite coatings containing of CS/HA the cracks are cut and smaller. When we exceed the weight ratio that been used in present work, the high flow amount of particles toward the cathode, which led to the irregular accumulation of particles on the surface of the cathode, causing a very weak adhesion of coating layer and then separation of large parts of the coating layer from the surface of the alloy after removing it from the solution. Generally, the addition of hydroxyapatite to the polymer reduce the presence of microcracks, this mean that the HA addition with (1,5,10 and 15) g/L to the CS polymer will be acceptable. These results are in agreement with reference [6].



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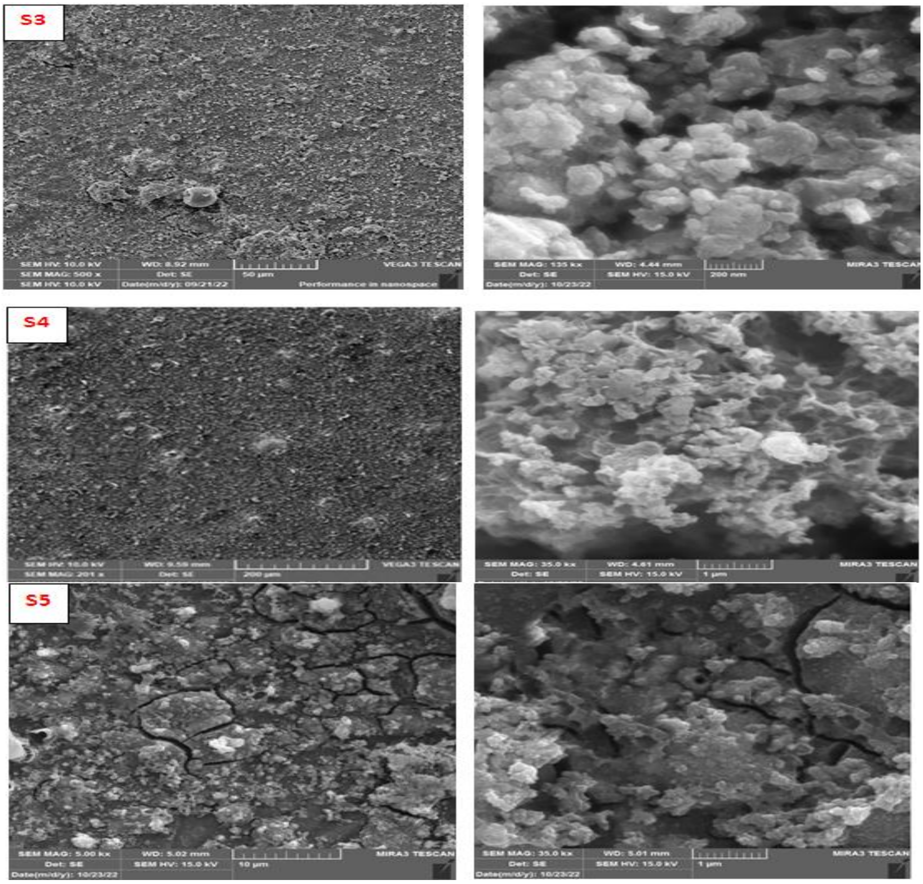

Fig. 2. SEM Image of AZ91 Coating Samples: a) coating only CS; b) coating CS with 1 (g/L)HAP; c) coating CS with 5 (g/L)HAP; d) coating CS with 10 (g/L)HAP; e) coating CS with 15 (g/L)HAP

4.2 Microhardness Results

Microhardness is an essential surface mechanical feature is widely utilized to evaluate the integrity and suitability of coatings for bioimplants. Figure 3 shows the average microhardness values of the samples that were measured. It can be seen, an increasing of the micro hardness value of composite coated samples with increasing of HA weight ratio. The sample that uncoated obtained the lowest microhardness (55 HV) whereas, the samples that coated with (CS/ 15 g/L HA) higher hardness (170 HV) compared with other specimens. These results are in agreement with references [7,8].

The reason of increasing the microhardness is an uniform distribution of reinforced HA particles, stable and dense coating layer on the modified specimens surface. The increase the surface hardness result increase in wear resistance under body fluid conditions and that prevents the deteriorating quickly of the surface. Moreover, higher hardness of coatings give metallic implants the ability to withstand of heavy loads and the significant increase of microhardness of coated samples keep the implant stability in the biological environment [9].

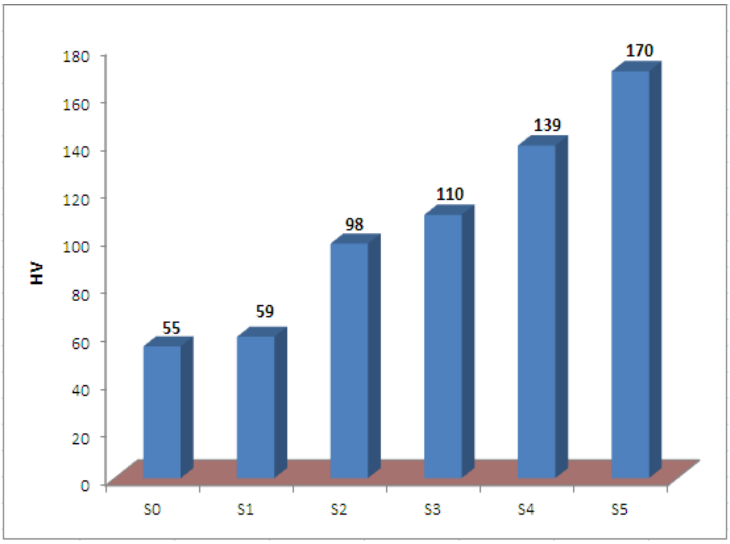

Fig. 3. The Micro Hardness of Bare And Coating AZ91 Mg Alloy

4.3 Hydrogen Evolution Result

To assess the behavior of corrosion for a long term of magnesium specimens can be use the hydrogen evolution experiment. The hydrogen was collected by using an inverted burette technique by completely covering the specimen in a ringer solution [10].

At the highest point, the burette's solution level was measured. The AZ91 specimens quickly begin to release hydrogen gas after immersed in the ringer solution, which that result from magnesium corrosion [11].

The hydrogen evolution from the AZ91 alloy specimens, whether they are bare, coated with CS, or coated with CS/ HA, in the immersion for 24 hours is shown in Figure 4. The uncoated AZ91 alloy released hydrogen quickly as expected, while the coated specimens produced a lesser volume of hydrogen. In comparison to the bare AZ91 specimen and coating specimens, the coating specimens of (CS/ HA) provided a good substrate protection and produced less hydrogen evolution.

The coated AZ91 alloy produced a less amount of hydrogen gas evolution compared to the bare AZ91 alloy. The (CS/ HA) coating specimens offered a good protection of substrate compare to the uncoating AZ91 specimen.

As a result of the breakdown of the magnesium substrate, hydrogen is released. It can be concluded that the AZ91 alloy corroded quickly at first, especially during the first immersion stage, and slowed down as time passed. This may be because of corrosion products that produced on the surface of alloys. In addition, the corrosion rate of the coated specimens were lower than the uncoated Mg specimen.

Moreover, the coated specimens have a lower corrosion rate than that uncoated specimens. The S5 specimen has the best protecting layer due to show a lower generation of H2 gas bubbles. These conclusions agree with the other researchers [12].

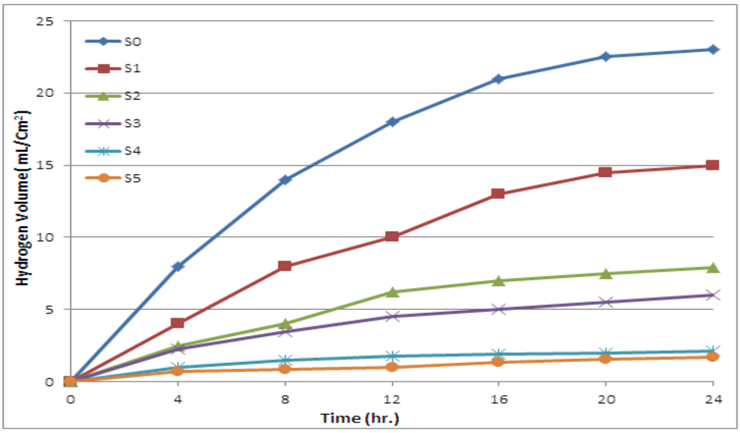

Fig. 4. Hydrogen Evolution of AZ91 with and Without Coated in Ringer Solution

4.4 4.4 pH-Measurement

To determine the pH values, samples were placed in ringer solution for 7 days at a temperature of 37°C ±1. The specimen is suspended in the solution without touching any surface. It varies with the immersion time, the pH of the solution is used to evaluate the corrosion resistance.

For 7 days of immersion, the pH values at the corrosive media were measured. Figure 5 shows the pH values of ringer solution with time of immersion. The substrates were degraded by the alkaline medium at the onset of immersion, that result the increased of the pH level of medium.

Under corrosion conditions, the coated specimens provided a good protection of the substrate compared to the uncoated specimen. The uncoated specimen had the greatest pH value due to the rapid generation of OH- and Mg+2 ions, which caused rapid deterioration. The S5 coated sample showed the least amount of pH increase of all the samples.

The coating specimens have a significant reduction in pH value compared with the uncoated specimen during the 7 days test period, and thus indicated a good corrosion resistance of the coating specimens compared with uncoated.

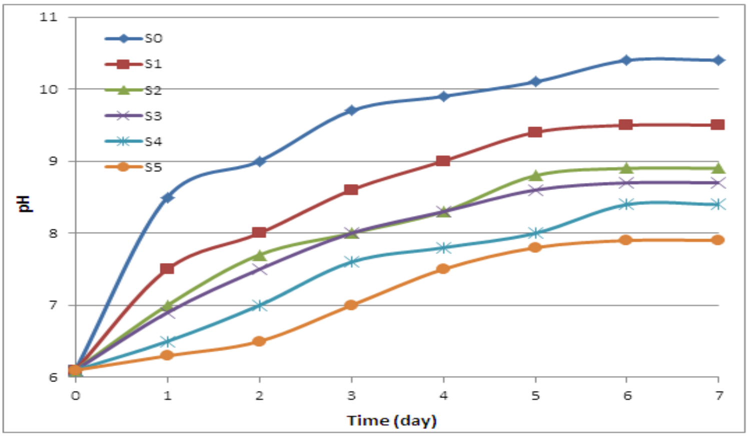

Fig. 5. The pH Changes In Ringer Solution With Time of Immersion In Days of With And Without Coating

4.5 Contact Angle (CA) Result

The contact angle test (CA) have been carried out to evaluate the wettability of the surface of specimens with and without coating. The surface has excellent wettability is referred it as hydrophilic when the contact angle lower than 90 degree. The surface is described as hydrophobic if the contact angle greater than 90 degree. In vivo, the cell adhesion is determined by the surface's wettability, whether its hydrophilicity or hydrophobicity.

In contrast to hydrophobic surfaces, the hydrophilic surfaces are better to allow of the biological responses of protein adsorption, cell adhesion, and proliferation [13].

Table 3 demonstrates the contact angle of ringer solution dramatically decreases from 90.401 on the uncoated specimen to the 45.879 on that coated surface (S5 specimen).

According to another studies [14,15], the reduce of CA on a surface coated of specimen is due to the CS strong adhesion and the fact that closing of pores and cracks makes it easier for water droplets to spread. The chitosanas a polymeric coating improved hydrophilicity of surface specimen therefore, enhance the cell attachment capability around the affected surface and the addition of HA to CS coating, can be attributed to decrease the contact angle by increase in surface roughness and resulting a good wettability [16].

The CA of CS With 15 g/L HA coating decreased to 45.879 degree, making the surface strongly hydrophilic and increasing its microroughness.

Table 3. Contact Angle Values of Samples

Sample Code	Contact angle in Ringer solution
S0	90.401 °
S1	82.578 °
S2	73.881 °
S3	61.101 °
S4	52.247 °
S5	45.879 °

5 Conclusion

1. Homogeneous distribution of coating materials, the CS polymer totally cover the surface area and HA, and no micro cracks developed on the surface of specimens are found from the SEM images.
2. The microhardness of the sample coating increase dramatically with increasing HA content due to the high hardness of bioceramic compared with the substrate and polymer. The microhardness of the CS + 15 (g/L) HA-coated is about 3 times higher than the uncoated specimen.
3. The composite coating is an effectively prevented the fluid from penetrating into the coating layer, which resulted the evolution of the least amount of hydrogen gas.
4. The uncoated specimen had the highest value of pH, compared with the coated specimens.
5. Decreasing in contact angle, good wettability and hydrophilic nature of coated specimen compared with uncoated specimen.

References

1. H. M. Wong, K. W. Yeung, K. O. Lam, V. Tam, P. K. Chu, K. D., Luk, K. M. Cheung, Biomaterials **31(8),** 2084-2096 (2010)

2. B. L. Luan, D. Yang, X. Y. Liu, G. L. Song, Corrosion of magnesium alloys pp. 541-564 (2011)
3. A. Di Martino, M. Sittinger, M.V. Risbud, Biomaterials **26(30),** 5983-5990 (2005)
4. H. R. Rezaie, L. Bakhtiari, A. Öchsner, Biomaterials and their applications (pp. 15-19) (Berlin, Germany: Springer International Publishing, 2015)
5. J. Toedt, D. Koza, K. Van Cleef-Toedt, Chemical composition of everyday products (Greenwood Publishing Group, 2005)
6. L. Morejón, et al, Biomaterials **72(2),** 345-352 (2005)
7. P. Bansal, G. Singh, H. S. Sidhu, Surface and Coatings Technology **401,** 126241 (2020)
8. R. Askarnia, S. R. Fardi, M. Sobhani, H. Staji, Ceramics International **47(19),** 27071-27081 (2021)
9. S. V. Dorozhkin, Coatings **12,** 1380 (2022)
10. B. Manne, H. Thiruvayapati, S. Bontha, R.M. Rangarasaiah, M. Das, V.K. Balla, Surface and Coatings Technology **347,** 337-349 (2018)
11. E.B. Öcal, Z. Esen, K. Aydınol, A. F. Dericioğlu, Materials Chemistry and Physics **241,** 122350 (2020)
12. H. M. Wong, K. W. Yeung, K. O. Lam, V. Tam, P. K. Chu, K. D. Luk, K. M. Cheung, Biomaterials **31(8),** 2084-2096 (2010)
13. S. M. Garner, E. A. O'Rear, S. S. Khajotia, F. L. E. Florez, Nanomaterials **10(6),** 1099 (2020)
14. A. Saberi, H. R. Bakhsheshi-Rad, S. Abazari,, A. F. Ismail, S. Sharif, S. Ramakrishna, F. Berto, Coatings **11(7),** 747 (2021)
15. N. Singh, U. Batra, K. Kumar, N. Ahuja, A. Mahapatro, Bioactive Materials **19,** 717-757 (2023)
16. M. Z. Elsabee, R. E. Morsi, A. M. Al-Sabagh, Biointerfaces **74(1),** 1-16 (2009)