



Research on super-hydrophobic surface of biodegradable magnesium alloys used for vascular stents

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ABSTRACT

Micro-nanometer scale structure of nubby clusters overlay was constructed on the surface of an AZ31 magnesium alloy by a wet chemical method. The super-hydrophobicity was achieved with a water contact angle of 142° and a sliding angle of about 5°. The microstructure and composition of the super-hydrophobic surface were characterized by SEM and FTIR. Potentiodynamic polarization and electrochemical impedance spectroscopy were used to evaluate the corrosion behavior, and the hemocompatibility of the super-hydrophobic surface was investigated by means of hemolytic and platelet adhesion tests. Results showed that the super-hydrophobic treatment could improve the corrosion resistance of magnesium alloys in PBS and inhibit blood platelet adhesion on the surface, which implied excellent hemocompatibility with controlled degradation.

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1. Introduction

Interest in metallic degradable biomaterials research has been growing in recent years, in which magnesium alloys are considered as a revolutionary biodegradable implant material. Compared with permanent metallic implants, such as stainless steel and cobalt–chromium based alloys, used for vascular intervention, this novel biodegradable material offers more physiological repair, reconstitution of local vascular compliance, and a temporary, limited, longitudinal, and radial straightening effect, including the possibility for growth [1]. It is expected to provide a temporary opening to a narrowed arterial vessel until the vessel remodels, and to disappear progressively thereafter.

Although results from early studies have shown their feasibility [2,3] and generated great expectation for researchers and clinicians, metallic biodegradable stents have not yet entered clinical practice because of their rapid degradation in an *in vivo* environment which would lead to implant failure by losing its mechanical integrity before complete restoration. It is necessary to control the corrosion rate of the material to match the remodeling process. As is known, the corrosion of magnesium alloys in aqueous environments can be expressed as the following reaction: $\text{Mg} + 2\text{H}_2\text{O} \rightarrow \text{Mg}(\text{OH})_2 + \text{H}_2$. This overall reaction includes both cathodic hydrogen evolution and anodic magnesium dissolution. Based on the above principle, if the magnesium substrate can be separated/protected from the aqueous environment, the fast degradation would be inhibited.

Wettability is an important characteristic of a solid surface. An interesting property of materials is super-hydrophobicity and the corresponding self-cleaning capacities. Super-hydrophobic surfaces with a water contact angle of more than 150° have attracted great attention owing to their promising potential applications, such as water repellency, lubricity, self-cleaning and antifouling properties [4–6]. As to the realization and regulation of super-hydrophobicity, relatively low surface energy and micro-nanometer binary morphology are, in general, necessary. Using such an approach, many researches on super-hydrophobic surfaces have made considerable progress in recent years, and super-hydrophobic films have been successfully fabricated on various engineering metallic materials, such as stainless steel, Cu, Al and Zn, among others [7–12]. However, few studies have been reported about super-hydrophobic treatment on magnesium alloys [13], especially for biomedical applications. Combined with super-hydrophobic property, magnesium alloys are expected to demonstrate their advantages by reducing the contact area of the metal substrate with the surrounding water environment and by reducing the corrosion rate. Moreover, the self-cleaning surface property could reduce the adhesion of protein, blood platelets and even smooth muscle cells, which would thus enhance hemocompatibility after implantation in blood vessels. Therefore, super-hydrophobic modification on biodegradable magnesium alloys for stent application is considered to be worthwhile.

Super-hydrophobicity on the surface of a material can be achieved by a combination of surface roughing and lowering of surface energy. Up to now, many methods have been developed, such as chemical etching, lithographic patterning, electrochemical deposition, sol–gel, layer-by-layer assembly and chemical vapor deposition, among others [14–19]. In the present work, fabrication of super-hydrophobic surface on an AZ31 magnesium alloy substrate was realized by a facile and efficient wet chemical

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method [20]. Surface analytical techniques, including SEM and FTIR, were used to study the characteristics of the super-hydrophobic surface formed on the AZ31 alloy. The corrosion behavior was investigated by potentiodynamic polarization and electrochemical impedance spectroscopy. The hemocompatibility of the super-hydrophobic surface was evaluated by means of a hemolytic test and a platelet adhesion test.

2. Experimental

2.1. Fabrication of super-hydrophobic surface

AZ31 magnesium alloy samples with a dimension of $\Phi 10 \text{ mm} \times 2 \text{ mm}$ were used in this study. The samples were ground with SiC abrasive paper up to 2000 grit, followed by ultrasonic cleaning in ethanol and distilled water, and finally dried in air. The samples were then immersed in 1% H_2SO_4 and 1% HF for 5 min, stirred in 20% H_2O_2 for 150 s, and finally rinsed with distilled water. After etching the samples were modified with stearic acid (0.05 M ethanol solution) at room temperature for 50 min.

2.2. Evaluation of super-hydrophobic surface

Morphologies of the super-hydrophobic surface were observed with field emission SEM (LEO SUPRA 35, Carl Zeiss, Germany). FTIR spectroscopic analyses were performed in reflection configuration with a PerkinElmer FTIR spectrometer in the 4000 to 400 cm^{-1} wavenumber range at a spectral resolution of 4 cm^{-1} using KBr pellet technique.

Contact angles were obtained using the sessile drop method with a JC2000A optical contact angle system (POWEREACH Inc., China). The drop image was stored by a video camera and the contact angle was calculated from the shape of the drop by an image analysis system. Distilled water drops were separately placed on each sample surface ($0.6 \mu\text{L}/\text{drop}$) and the corresponding contact angles were measured subsequently. Three different regions on the surface were used and the measured results were averaged to reduce deviation.

2.3. Electrochemical test

The electrochemical corrosion behavior was investigated by potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) using a PARSTAT 273A potentiostat controlled by the PowerSuite software. A three-electrode cell featuring a Pt counter electrode and a saturated calomel reference electrode (SCE) was employed. The experiments were carried out using phosphate buffered saline solution (PBS, 0.14 M NaCl, 1 mM KH_2PO_4 , 3 mM KCl, 10 mM Na_2HPO_4 , pH = 7.4) at 37°C .

The samples were allowed to stabilize at their open circuit potential (OCP) for 30 min before the measurements were started. Potentiodynamic polarization tests were conducted at a sweep rate of 0.5 mV/s within a scan range of $\pm 0.25 \text{ V}$ with reference to OCP. Impedance experiments were carried out using a 10 mV root-mean-square perturbation from 100 kHz to 10 mHz. Fitting was performed with the ZSimpwin software. All the electrochemical tests were conducted in triplicate in order to ensure the reproducibility of the results.

2.4. In vitro hemocompatibility test

Venous blood was obtained from a healthy volunteer. Blood samples were anti-coagulated with acid citrate dextrose and processed to yield platelet-rich plasma (PRP). The PRP was then centrifuged and any remaining red blood cells were removed, and the prepared PRP contained about $2.5\text{--}3 \times 10^8$ platelets/mL.

Platelet adhesion was conducted using standard blood-material interaction tests [21]. PRP was added on top of samples in 24-well plates until the entire surface was covered. Samples were incubated for 1 h at 37°C in a humidified 5% CO_2 atmosphere. Thereafter, the samples were

rinsed with PBS carefully to remove the weakly adherent platelets. Adherent platelets were then fixed in 2.5 vol.% of glutaraldehyde solution prepared in phosphate buffered saline (PBS, pH 7.4) for 2 h, and dehydrated using a graded ethanol series (50, 60, 70, 80, 90 and 100 vol.% of ethanol) for 10 min each. The fluorescent adhesion assay [22] was used to determine platelet adhesion with FITC staining and imaged on a fluorescence microscope (Eclipse 80i, Nikon, Japan). Three images were taken in different randomly selected substrate locations for each sample. The number of adherent platelets was determined using image analysis software and the mean number of platelets per mm^2 was calculated.

For the hemolytic test by reference to ASTM F-756-08 and ISO/TR 7405:2008, samples were immersed in centrifuge tubes containing 10 mL of PBS with an immersion ratio of $1.25 \text{ cm}^2/\text{mL}$ (total surface area of sample versus volume of immersion solution) as a test group. PBS used as a negative control group, and the distilled water used as a positive control group were also added in centrifuge tubes with the same volume. Then all the centrifuge tubes were incubated at 37°C in a humidified 5% CO_2 atmosphere for 30 min. A volume of 0.2 mL of diluted blood was then added to each tube, and the mixtures were incubated for 60 min. The tubes were centrifuged for 5 min at 3000 r/min, and the supernatants were extracted. 100 μL of liquid from each tube was transferred to a 96-well plate for spectroscopic analysis at a wavelength of 545 nm. Values obtained for 3 replicates of samples were then calculated. The hemolytic ratio was calculated according to the following formula:

$$\text{Hemolytic ratio} = (D_t - D_{nc}) / (D_{pc} - D_{nc}) \times 100\%$$

where D_t , D_{nc} and D_{pc} represent the absorbance of the sample, the positive control and the negative control respectively.

Statistical analysis was conducted with SP10.0. Differences between groups were analyzed using one-way ANOVA followed by Tukey's test.

3. Results and discussion

3.1. Characterization of the super-hydrophobic surface

The contact angle (CA) of a water droplet strongly depends on the degree of hydrophobicity of the surface. Fig. 1 shows the photographs of water droplets on surfaces of untreated and super-hydrophobic samples. It can be seen that the wettability of the surface is significantly changed after the AZ31 substrate was modified by super-hydrophobic treatment. The contact angle of the untreated AZ31 sample is $76.1^\circ \pm 1.7^\circ$, indicating a typical hydrophilic material, while the super-hydrophobic sample exhibited a high contact angle of $141.8^\circ \pm 0.76^\circ$. An increase in hydrophobicity could minimize the adhesive interaction between the water drop and the solid surface, and hence increase the contact angle. At the same time, the sliding angle of the super-hydrophobic surface was lower than 5° . In addition, the samples were kept at ambient temperature for 2 months, and no decrease in water contact angle was observed and no contamination such as dust or griminess was observed.

Fig. 2 shows the typical morphology of a super-hydrophobic surface. A rough and porous structure was observed on the surface of the sample. Under high magnification it can be seen that the surface is covered by nubby clusters which exhibited an interesting structure with nanoscale protuberances. Such micro-nanometer scale structure and cavity on the surface played an important role in trapping air. The low surface energy of the materials as well as the rough micro-nanometer binary structure of the surface are crucial for realization of super-hydrophobicity.

From the Cassie and Baxter equation [23] as follows, the area fraction of trapped air within this structure could be deduced. The equilibrium contact angle of the $\text{C}_{18}\text{H}_{35}\text{O}_2^-$ coated smooth surface of a magnesium alloy has been reported to be about 109° (taken as θ_0)

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