# Design of TEOS-GPTMS sol-gel coatings on rare-earth magnesium alloys employed in the manufacture of orthopaedic implants

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**Abstract.** In the present work hybrid sol-gel coatings were synthesized on different magnesium alloys with potential interest in the fabrication of orthopaedic implants. Hybrid sols were obtained from a mixture of the inorganic precursor tetraethoxysilane (TEOS) and the organic precursor 3-glycidoxypropyltrimethoxysilane (GPTMS), employing ethanol as solvent and acetic acid as catalyst. The characterization of the sols was performed using pH measurements, rheological tests and infrared spectroscopy (FTIR) for different aging times. On the other hand, the coatings were characterized by scanning electron microscopy (SEM), while the corrosion resistance was evaluated using anodic polarization in SBF solution at 37±2°*C*. The results confirmed that, under specific conditions, uniform and homogeneous sol-gel coatings were obtained, which enhanced the corrosion resistance so that the corrosion current density was reduced in about two orders of magnitude with regard to the parent alloy.

## 1. Introduction

In biomedicine, metallic materials perform an essential role as biomaterials for the fabrication of temporary orthopaedic implants, assisting during regeneration of bone tissue damaged. For this purpose, AISI 316L stainless steel and Co-Cr and Ti alloys has been conventionally employed due to their excellent combination of mechanical properties and corrosion resistance. Nevertheless, one of the main disadvantages of the use of these alloys is their high mechanical properties (density, elastic modulus, and compressive yield strength), which increases the tendency to generate a stress shielding phenomenon between the implant and bone tissue. In this regard, rare-earth magnesium alloys are recently considered potential candidates to replace those alloys since their mechanical properties are close to those of the human bone so that, in theory, might reduce the stress shielding difficulty [1,2]. Moreover, magnesium alloys exhibit excellent biocompatibility, in which rare earth alloying elements provide anticarcinogenic properties to the alloy [3].

However, the main limitation of magnesium alloys for their implementation as biomaterial is the high degradation rate of magnesium as element in physiological environments, which may bring negative consequences such as loss of the mechanical integrity of the implant before the bone has healed. Further, according to its corrosion mechanism, magnesium degradation also generates hydrogen gas bubbles, which, in case of accumulation, can lead to undesired subcutaneous swelling and necrosis of the adjacent tissue [4].

Aiming to improve the corrosion resistance of magnesium alloys, synthesis of hybrid sol-gel coatings (mixture of organic and inorganic precursors) have arisen as one of the most promising

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alternatives due to its convenient adhesion to the metallic substrate, low cracking susceptibility, high density and flexibility [5]. The latter has been associated with the presence of organic precursors, which promote crosslinking of the sol-gel network and reduces both temperature and time during the curing process, this being an important factor for alloys with a low melting point like magnesium ones [6].

Based on these statements, the aim of the present work was to design hybrid sol-gel barrier coatings to enhance the corrosion resistance of the ZE41 rare-earth magnesium alloy.

## 2. Experimental procedure

The material used in the present investigation was the ZE41 magnesium alloy. The nominal composition (%wt) of the alloy is: 3,5-5,0 Zn; 0,4-1,0 Zr; 0,75-1,75 RE (La,Ce,Ga); 0,15 Mn and balance Mg. Hybrid sols were prepared from a mixture of the inorganic precursor tetraethoxysilane, TEOS, and the organic precursor 3-glycidoxypropyltrimethoxysilane, GPTMS, in 3:1 molar proportion, employing ethanol as a solvent and acetic acid as catalyst. Sols were characterized by pH measurements, rheological tests and Fourier Transform Infarred (FTIR) spectroscopy for different ageing times in order to study the hydrolysis and condensation process. Later, sol-gel coatings were obtained by deposition of the sol following the dip-coating route and then were cured at 120$^{o}C$ for 2 hours. Coatings were characterized using scanning electron microscopy (SEM), while their corrosion resistance was evaluated by anodic polarization test in simulated body fluid (SBF) solution at 37±2$^{o}C$.

## 3. Results

### *3.1. Characterization of hybrid sols*

Figure 1 comprises the results of the hybrid sols characterization. The evolution curves of viscosity and pH for different aging times are given in Figure 1(a). Hybrid sols showed a moderated increment in viscosity until a critical point that was reached at the fifth day, when the viscosity suffered an abrupt slope change associated with the definitive progress of the condensation reactions (beginning of the gelation state). On the other hand, pH values of sol remain constant in 5, from the first day, due to the employment of acetic acid (weak acid) as catalyst, which stabilizes the acidity of the sol.

Regarding the infrared spectroscopy results, Figure 1(b) shows the FTIR spectra of the sol for different aging times. Vibration bands related to the O-H and C-H (stretching and bending) can be observed at wavenumber of 3400-3200$cm^{-1}$ ($\upsilon$(O-H)), 3000-2900$cm^{-1}$ ($\upsilon$(C-H)), 1650$cm^{-1}$ ($\delta$(O-H)) and 1500-1300$cm^{-1}$ ($\delta$(C-H)). On the other hand, Figures 1(c-e) comprises the deconvolution analysis of the region 1250-1000$cm^{-1}$, where the bands related to Si-O-Si, Si—OH and Si-C bonding are masked. It can be noticed the presence of bands associated with: a) the symmetric and asymmetric vibrations of Si-OH bonding centred at 1200 and 1170$cm^{-1}$, which increases in intensity with the ageing time indicating that the hydrolysis of the precursors is occurring as part of the gelation process; the vibrations of the Si-O-C bonding (1100 and 1070$cm^{-1}$) related to the presence of the no-hydrolyzed precursor that decrease in intensity, as expected; finally, the vibration band centred at 1040$cm^{-1}$ was related to the formation of Si-O-Si bonding, which increases in intensity associated to the advance of the condensation reactions.

### *3.2. Characterization of the hybrid sol-gel coatings*

Electron micrographs of the coatings synthesized on the ZE41 magnesium alloy at different aging times are shown in Figure 2. For the shortest aging time (2 hours), the coating revealed low uniformity being the microstructure of the alloy still visible (Figure 2(a)). Conversely, after 3 days it was possible to obtain homogeneous coating with a good wettability and virtually free of cracks (Figure 2(b)). Further, longer aging time (5 days) resulted in high viscosity sols, which deposition originates thicker, cracked coatings, attributed to the generation of internal stress during the curing treatment (Figure 2(c)).

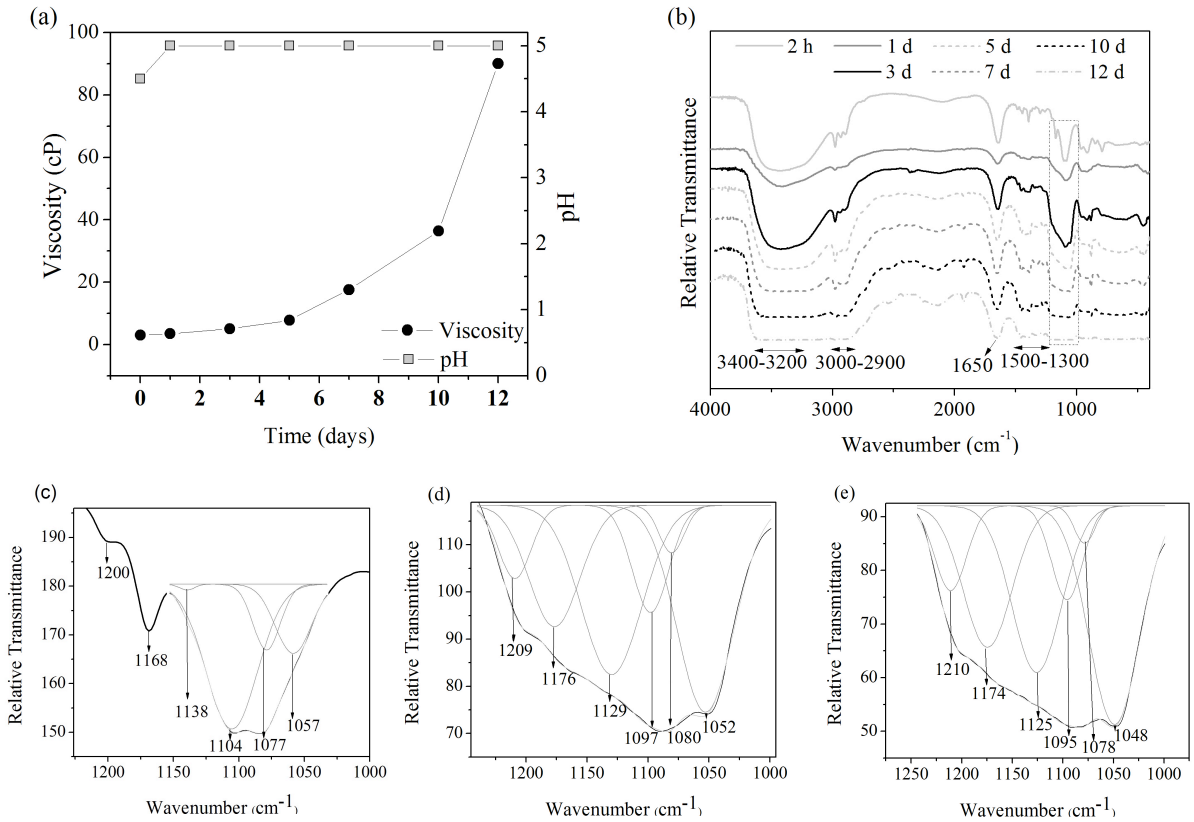



**Figure 1**. (a) Evolution of viscosity and pH of the TEOS-GPTMS sol versus aging time. (b) General FTIR spectrum. (c-e) Deconvolution analysis of the region 1250-1000$cm^{-1}$.

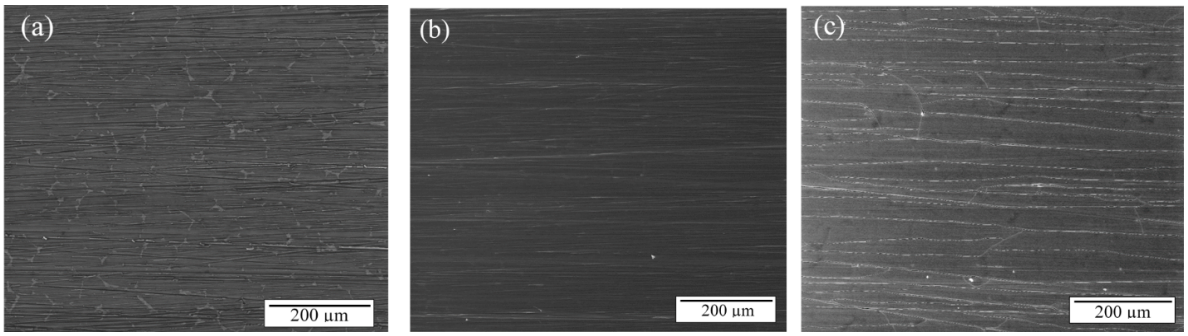



**Figure 2.** Surface electron micrographs of the hybrid sol-gel coatings for different aging times: (a) 2 hours, (b) 3 days and (c) 5 days.

*3.3. Evaluation of the corrosion resistance of the coatings*

Figure 3 shows the anodic polarization curves of the ZE41 alloy and the hybrid sol-gel coatings synthesized at different aging times. In general, the hybrid sol-gel coatings enhanced the corrosion resistance of the alloy, except for the shortest aging time (2 hours). In this case, the coating did not offer a convenient protection, showing similar values of corrosion current density with the alloy (Table 1). On the other hand, the best corrosion behaviour was exhibited by the coating synthesized at 3 days of aging, which corrosion current density was reduced by about two orders of magnitude. However, for longer times, the cracks favoured the diffusion of the electrolyte through the coating, diminishing its barrier properties.

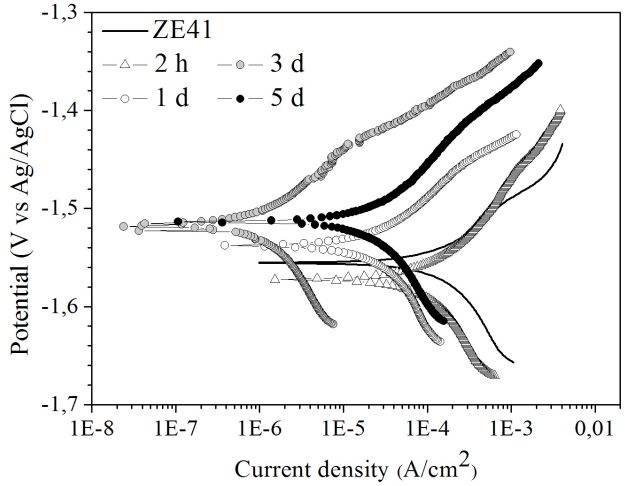



**Figure 3**. Anodic polarization curves of the ZE41 magnesium alloy and the hybrid sol-gel coatings obtained at different aging times.

**Table 1**. Electrochemical parameters obtained from anodic polarization curves.

| | Corrosion potential (V vs Ag/AgCl) | Corrosion current density ($A/cm^2$) |
|---|---|---|
| ZE41 | -1,55 | 1,4E-4 |
| 2h | -1,57 | 8,8E-5 |
| 1d | -1,54 | 1,7E-5 |
| 3d | -1,51 | 1,0E-6 |
| 5d | -1,51 | 2,4E-5 |

## 4. Conclusions

The results confirmed that the employment of TEOS-GPTMS systems and under specific ageing conditions allows obtaining uniform and homogeneous sol-gel coatings, with no evidence of cracking, which enhanced the corrosion resistance properties so that the corrosion current density was reduced up to two orders of magnitude with regard to the ZE41 alloy.

Ageing time played a key role in the morphology and barrier properties of the hybrid sol-gel coating. In this regard, coatings synthesized at shorter aging times did not improve the corrosion resistance, due to the hydrolysis-condensation reactions were still not significant. By contrast, for extended aging times, the high viscosity of the sol resulted in coatings with presence of cracks and diminished corrosion properties.

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