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# Coatings on implants: Study on similarities and differences between the PCL coatings for Mg based lab coupons and final components

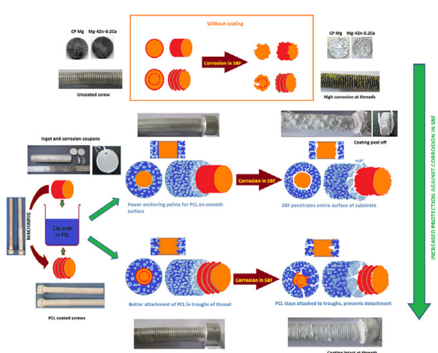
Deepa B. Prabhu [a], P. Gopalakrishnan [b], K.R. Ravi [a,b,*]

[a] *Structural Nanomaterials Lab, PSG Institute of Advanced Studies, Coimbatore 641004, Tamil Nadu, India*
[b] *Department of Metallurgical Engineering, PSG College of Technology, Coimbatore 641004, Tamil Nadu, India*

## HIGHLIGHTS

- Corrosion resistance of pure Mg, uncoated and PCL coated Mg-4Zn-0.2Ca alloy screws are investigated.
- Corrosion of coated Mg alloys proceeds via penetration of medium through pores in the polymer and degradation of substrate.
- PCL layer peels off faster in CP Mg than in Mg-4Zn-0.2Ca due to the faster corrosion rate of CP Mg.
- PCL coating adheres stronger to threaded portion of fabricated screws than smooth regions upon immersion in SBF.
- Corrosion resistance of a coated fully threaded screw is better than that of a partially threaded screw.

## GRAPHICAL ABSTRACT



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## ABSTRACT

Corrosion behaviour of polymer coated Mg alloy screw is compared with a laboratory coupon with emphasis on the adhesion of coating to surface features such as threads. The corrosion behaviour of poly (ε-caprolactone) (PCL) coated commercial pure Mg (CP Mg) and Mg-4Zn-0.2Ca alloy in simulated body fluid (SBF) is investigated. CP Mg with a high corrosion rate (8.426 $mmyr^{-1}$) formed large amount of corrosion products on the surface which pushed out the PCL layer. In contrast the Mg-4Zn-0.2Ca alloy with a corrosion rate of 2.481 $mmyr^{-1}$ held the PCL coating intact for up to 72 h. Fully and partially threaded screws of the Mg-4Zn-0.2Ca alloy were fabricated and coated with PCL. It was found that pH variation of the medium depends on PCL adhesion to screw, which was better in the threaded regions than in smoother areas. As a result, the fully threaded screws showed slower pH rise than partial threaded ones. The crests and troughs of the threads act as anchoring points for the polymer. It was found in the current study that the increased adhesion of PCL coating to threaded Mg alloy substrate dominates over the increased corrosion rates of threaded surface.



## 1. Introduction

Magnesium and its alloys degrade in the human body via an electrochemical reaction [1–3] and are good candidates for temporary orthopaedic fixture devices [4]. Alloying with essential elements such as Ca, Zn and Mn increases biocompatibility, corrosion resistance and reduces

* Corresponding author.
*E-mail address:* krr@psgias.ac.in (K.R. Ravi).

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**Table 1**
Chemical composition of the as cast Mg-4Zn-0.2Ca alloy.

| Element | Mg | Zn | Ca | Al | Si | Mn |
|---|---|---|---|---|---|---|
| Quantity (wt. %) | 96.01 | 3.6 | 0.15 | 0.017 | 0.012 | 0.02 |

side effects of the implant [5–7]. Though corrosion resistance of magnesium can be increased by alloying [6,8–10] or mechanical and/or heat treatment [11,12], the initial high electrochemical activity when in contact with the body fluids has to be avoided to delay the beginning of degradation. Surface modifications and coatings offer a barrier to the contact between the alloy and the corrosive medium and delay the start of deterioration [2,8,13,14]. Such biocompatible coatings are used even in titanium based permanent implants and offer better corrosion and wear resistance along with easier osseointegration [15–18].

Compared to coatings of metals or ceramics, biodegradable and resorbable polymers offer added advantages of ease of synthesis, blend compatibility and possibility of incorporating drug delivery to avoid infection and implant rejection [19–36]. The products formed on degradation of these polymers are harmless to the human body and are eliminated by the citric acid cycle [30]. PCL is an FDA approved, resorbable polymer with good solubility, blend-compatibility and body stability for about 1 year used successfully in drug-delivery devices [37]. In addition, degradation kinetics, mechanical properties, pore size and stress crack resistance of PCL can be tuned by blending with other suitable polymers. The degradation mechanism of PCL in the human body is not enzymatic [19] and proceeds by hydrolytic cleavage and phagocytosis [30]. Use of PCL in porous composite scaffolds [38,39] show reasonable mechanical properties and bioactivity and hence is recommended as a candidate material for use in the repair and regeneration of non-weight-bearing bones.

Similar to other polymers, PCL also tends to absorb large quantities of water on immersion in body fluids and bulges and/or peels off when applied on Mg alloys [35]. This effect is pronounced as the coating thickness increases, and is mainly attributed to the increased defects in the layer and subsequent corrosion of substrate with formation of magnesium hydroxide and hydrogen evolution [20]. It was also found that the corrosion resistance increases with concentration of polymer [36], and presence of multiple coatings [23]. In vivo studies [40] of PCL coated AZ91 alloy indicated reduced degradation rate and retention of bulk mechanical properties, with higher bone regeneration rates compared to bare alloy. Research on multi-layer plasma/polymer coating developed by Bakhsheshi-Rad [22] on Mg-Ca alloy showed that the bonding strength of the PCL coating stems from the penetration of the polymer into the nano porous plasma coating on the Mg alloy and provides significant protection against corrosion. These studies indicate that the parameters that affect the corrosion behaviour of the base material such as its size, shape, surface area and surface finish, also might have profound effect on the adhesion of the coating.

To understand these parameters further, consider a commonly used orthopaedic implant such as a compression plate with screws. The effect of polymer coating on the plate and screws will be different due to its different surface features. Though plate geometry can be modelled closely by a flat coupon, there could be vast differences in understanding the behaviour of a screw based on experiments conducted on a flat coupon. The use of polymer coatings over a threaded geometry adds to the complexity of the system due to the formation of corrosion products in the interface of the two materials. The threaded portion of the screw is responsible for its anchorage to the bone, and fast degradation of the threads might result in loosening of the implant before sufficient healing of the bone. Most of the in vitro tests on corrosion of Mg alloys are reported for laboratory coupons. Rod geometries are typically used for biomechanical tests such as pull-out strength or for majority of the in vivo studies. Investigations on threaded screws are limited to in vivo studies in small animal models [41–44] where the key focus was the integration of threaded implant to the bone and biocompatibility of the material itself. The surface structure was found to be critical in the mechanical properties of the alloy and the corrosion at the threaded flanks was found to result in irregular, hole-shaped degradation [41]. Recently, biomechanical properties and short to long term fracture fixation and osseointegration studies of the MAGNESIX® screw has been published [45]. Though there is significant difference between the in vivo and in vitro corrosion behaviour of Mg alloys due to the complex body environment that cannot be reproduced in a laboratory, it is important to understand the corrosion of such threaded screws in simulated body environments so that a better approximation than the lab coupons is obtained. Though these factors are addressed in corrosion of structural materials, such studies are not commonly undertaken in the case of biodegradable implant materials. Hence the authors have attempted to study the corrosion behaviour of PCL coated Mg alloy in this work on machined components in the form of partial and full threaded screws with preliminary studies on disc shaped laboratory corrosion coupons. Moreover the critical factor in sustaining this improved corrosion resistance, namely the adhesion of PCL coating to the Mg substrate is also addressed in this work.

## 2. Experimental details

### 2.1. Fabrication of the alloy and characterization

Commercial pure Mg (CP Mg), Zn and Mg-30% Ca master alloy were melted in the desired proportions under protective argon atmosphere to prepare the Mg-4Zn-0.2Ca alloy. The melt was held at 750 °C for 10 min to ensure proper mixing and then poured into stainless steel moulds with sulphur dusting to avoid oxidation. Chemical composition of the cast alloy was determined by inductively coupled plasma optical emission spectroscopy (ICP-OES) in a Perkin Elmer Optima 2100 DV instrument and is given in Table 1. Metallographic specimens of 10 mm thickness and 30 mm diameter were prepared from the casting as per standard procedure. The samples were etched with acetic picral to reveal the microstructure and observed in a Carl Zeiss Axioscope A1 microscope. The surface was also analyzed with an Environmental Scanning Electron Microscope (ESEM, Zeiss EVO18), equipped with an energy-dispersive spectroscopy (EDS) attachment for identification of various elements present. Surface roughness of the specimen is analyzed with a Mitutoyo SJ410 with a cut off $\lambda_c$ of 0.8 μm at 0.5 mm/s scan speed over a length of 4 mm. Average of three measurements is presented.

Polycaprolactone (Average Mn of 80,000) (Sigma Aldrich) was dissolved in dichloromethane to obtain 1%, 2.5% and 5% (w/v) solutions. Dip coating was employed since this method can be extended to final screw shaped components also. Initial optimization of dip coating was carried out at these three concentrations to obtain a coating of PCL on the Mg alloy as per the following procedure: The metallic coupons were cut from the as cast ingots with dimensions of 30 mm diameter and 10 mm thickness. The coupons were polished with SiC sheets up to 1200 grit followed by disc polishing with diamond paste. The coupons were degreased, washed in distilled water, dried in warm air and were dipped in the PCL solution for 10 s. The PCL solution was maintained in a closed glass beaker at 30 °C on a hot plate with constant

**Table 2**
Chemical composition of the prepared simulated body fluid.

| Species | Concentration (mg/l) |
|---|---|
| Magnesium, Mg | 14.6 |
| Calcium, Ca | 68 |
| Potassium, K | 242 |
| Sodium, Na | 4350 |
| Chloride, $Cl^-$ | 6998 |
| Sulphate, $SO_4^{2-}$ | 603 |
| Phosphate, $(PO_4)^{3-}$ | 151 |
| Bicarbonate, $HCO_3^-$ | 450 |