

## *Original*

Scharnagl, N.; Mueller, P.:

**Pre-treatment and organic coating of Al free Mg alloy for  
controlling degradation rates**

Materials Science Forum, Light Metals Technology 2015 (2015)  
Trans Tech Publications

DOI: [10.4028/www.scientific.net/MSF.828-829.327](https://doi.org/10.4028/www.scientific.net/MSF.828-829.327)

# Pre-treatment and Organic Coating of Al free Mg Alloy for Controlling Degradation Rates

NICO Scharnagl<sup>1,a\*</sup>, PHILIPP Mueller<sup>2,b</sup>

<sup>1</sup>Helmholtz-Zentrum Geesthacht Centre for Materials and Coastal Research GmbH, Institute of Materials Research - MagIC, Max-Planck-Strasse 1, D-21502 Geesthacht, Germany

<sup>2</sup>Helmut Schmidt University, University of the Federal Armed Forces Hamburg, Holstenhofweg 85, D-22043 Hamburg, Germany

<sup>a</sup>nico.scharnagl@hzg.de, <sup>b</sup>m777506@hsu-hh.de

**Keywords:** surface treatment, polymeric coating, biomaterial, Mg alloy.

**Abstract.** Biodegradable implant material for medical applications has to fulfil specific therapeutic tasks. For our investigations, synthetic polymers, i.e., polyurethanes (PUR) and polyetherimide (PEI), were used. Both systems have been used to coat an Al-free Mg alloy. Characterization of materials was performed by infrared spectroscopy (IR), spark spectral analysis, microscopy and electrochemical impedance spectroscopy (EIS). Electrochemical investigations of the different treated samples in aqueous NaCl and Hank's Balanced Salt Solution indicate specific response of the polymer/substrate system to corrosion attack.

## Introduction

Surface modification is a very useful tool in manipulating surface characteristics and is even more important when it comes to implantable metallic biomedical materials. Specific interactions with in vivo environments mostly occur on the surface or subsurface, and these phenomena are often unpredictable and uncontrollable [1]. However, the material has to fulfil specific therapeutic tasks and, over time, subsequently degrade while it is harmlessly excreted from the body. For a long time natural polymers have been used in medical applications. Synthetic polymers are valuable also and have the advantage to allow tailoring of properties such as mechanical strength and degradation behaviour [2]. PURs are versatile polymer systems as it is possible to tailor their mechanical properties and their hydrolytic degradation profile [3]. For biomedical applications, the biodegradability as well as the mechanical properties of the polymers during the course of degradation are of importance. For cardiovascular applications polymer systems have to prevent inflammation or restenosis. Therefore, PEI is a suitable polymer that offers functionalization by chemical reaction at the surface [4-6].

## Experimental procedures

An extrusion molded Mg alloy with the composition given in Table 1 was used for the investigations. A SPECTROLAB spark discharge optical emission spectroscopy device (SD-OES) with spark analyser vision software was used to determine the average elemental compositions on the surfaces of as-received and cleaned specimens. The elemental composition obtained is the average of three different runs for each specimen.

Table 1. Composition (wt.%) of as received Mg alloy determined by spark analysis.

Ca	Al	Zn	Ce	Mn	Fe	Nd	Pr	La	Mg
0.419	< 0.03	5.72	0.34	0.03	< 0.006	0.53	0.07	0.255	93.55

The pre-treatment consisted of alkaline degreasing of the metallic specimen for 1 minute followed by etching with different organic and inorganic acids while concentration and treatment time were varied (30, 60 and 120 s.). The specimens (11 mm diameter, 3 mm thickness) were weighed before and after cleaning using a Mettler AC 100 electronic balance, and the weights were recorded. The

difference in weight before and after cleaning (weight loss) gave the material removed in micrometer ( $\mu\text{m}$ ) as calculated from  $W = (w * 10^4)/(\rho * A)$  where  $W$  is the material removed in  $\mu\text{m}$ ,  $w$  is the weight loss in g,  $\rho$  is the density in  $\text{g}/\text{cm}^3$ ,  $A$  is the area in  $\text{cm}^2$ , and  $10^4$  is a unit conversion factor.

For coating a 1K PUR (1 component) and a 2K PUR (2 component) system were selected and compared to PEI as well as to the uncoated alloy. While the PUR coating was carried out by cross-linking of the mixture of the components on the substrate, PEI was dissolved in N,N'-dimethylacetamide (10 wt.-%) to dip-coat the substrate.

Electrochemical studies were carried out using a computer controlled potentiostat/frequency response analyser (Gill AC, ACM Instruments, UK) to evaluate the performance of the polymer coatings on the Mg alloy. A typical three electrode system was used consisting of a platinum mesh as counter electrode, an Ag/AgCl reference electrode and the specimen ( $19.6 \text{ mm}^2$  exposed area) as working electrode. The experiments were conducted in aqueous 0.1 molar NaCl solution at room temperature and, except the 2K PUR, in Hank's Balanced Salt Solution (HBSS) at  $37^\circ \text{C}$  (composition s. Table 2). Prior to the experiments the samples were exposed for 30 min to electrolyte to establish a relatively stable open circuit potential. Electrochemical impedance spectroscopy (EIS) experiments were performed at open circuit potential with AC amplitude of  $\pm 10 \text{ mV}$  over the frequency range of 30 kHz to  $10^{-2} \text{ Hz}$ . The EIS tests were repeated after fixed exposure periods between 0.5 h and 24 h.

For the IR investigations a Bruker TENSOR FTIR spectrometer equipped with an ATR facility was used.

Table 2. HBSS composition according to [7].

Component	Molecular Weight (Da)	Concentration (mg/L)
Potassium Chloride (KCl)	75	400
Potassium Phosphate monobasic ( $\text{KH}_2\text{PO}_4$ )	136	60
Sodium Bicarbonate ( $\text{NaHCO}_3$ )	84	350
Sodium Chloride (NaCl)	58	8000
Sodium Phosphate dibasic ( $\text{Na}_2\text{HPO}_4$ ) anhydrous	142	48
D-Glucose (Dextrose)	180	1000

## Results and Discussion

According to earlier studies of the pre-treatment of Mg alloys [8, 9] a number of inorganic (nitric acid, sulphuric acid, phosphoric acid), and organic acids (acetic acid, citric acid, oxalic acid) were selected for evaluation of the morphology and composition of the treated Mg alloy. Fig. 1 shows the amount of material removed by some selected pre-treatments. The removal increases with time and concentration for all agents used. Additional evaluation by SEM, IR and SD-OES lead to the pre-selection of acetic acid and phosphoric acid as pickling agents.

Table 3. Composition (wt.-%) of the Mg alloy after 60 s. pre-treatment with acetic and phosphoric acid determined by SD-OES.

	Ca	Al	Zn	Ce	Mn	Fe	Nd	Pr	La	Mg
untreated	0.42	< 0.03	5.72	0.34	0.03	< 0.006	0.53	0.07	0.26	93.55
100 g/L CH <sub>3</sub> COOH	0.44	< 0.03	6.24	0.48	0.03	< 0.006	0.67	0.09	0.33	93.01
300 g/L CH <sub>3</sub> COOH	0.39	< 0.03	6.17	0.44	0.03	< 0.006	0.61	0.08	0.29	93.14
40 g/L H <sub>3</sub> PO <sub>4</sub>	0.43	< 0.03	7.21	0.63	0.03	< 0.006	0.81	0.12	0.38	92.04
60 g/L H <sub>3</sub> PO <sub>4</sub>	0.46	< 0.03	8.78	0.74	0.03	< 0.006	0.94	0.13	0.47	90.44
80 g/L H <sub>3</sub> PO <sub>4</sub>	0.45	< 0.03	9.73	0.77	0.03	< 0.006	0.95	0.13	0.48	89.50

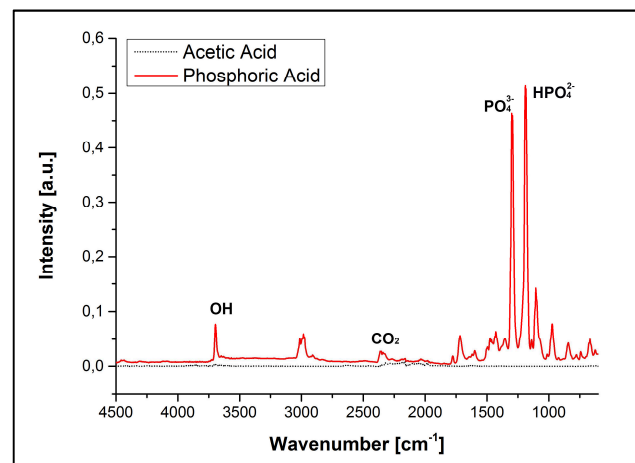
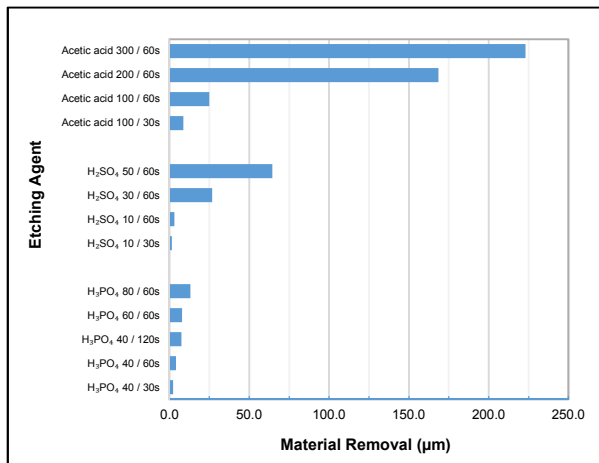


Fig. 1. Material removal by various etching procedures.

Fig. 2. ATR-IR of acetic and phosphoric acid treated Mg alloy surface.

For acetic acid the highest material removal during pre-treatment is observed. Therefore, most of the impurities on the surface should be removed. As shown by the SD-OES data in Table 3, the composition of the material is in the range of statistical variations of the untreated alloy and therefore seems to be homogenous. Compared to acetic acid the removal of material is also high for the use of sulphuric acid. For sulphuric acid a huge increase in the Zn concentration is observed which might be caused by reduced solubility of build zinc sulphate in the sulphuric acid solution. The Zn increase also could be observed for phosphoric acid treatment but with lower values which are in an acceptable range (Table 3). Infrared spectra of the alloy surface after its treatment with phosphoric and acetic acid are shown in Fig. 2. Unfortunately, phosphates have been built during etching and still remain on the surface after washing steps by distilled water and drying by a stream of hot air. For variations in concentration of the phosphoric acid this behaviour did neither qualitatively nor quantitatively change. For the treatment with acetic acid no residuals could be detected.

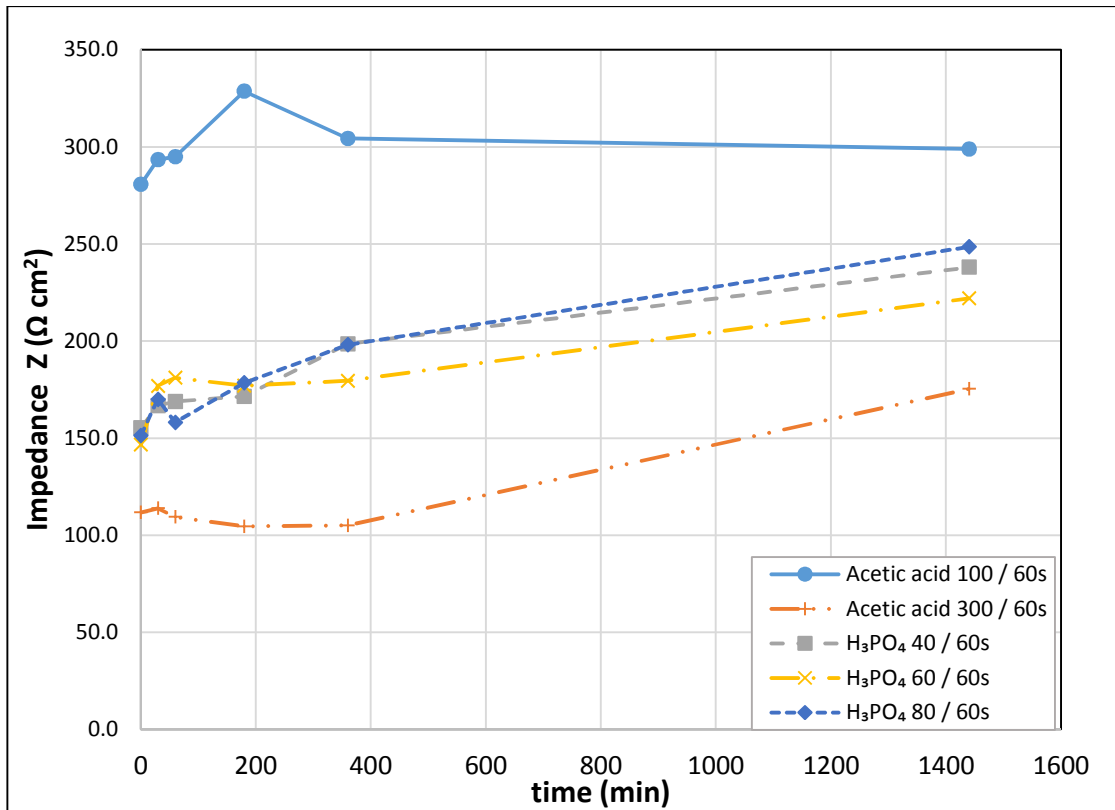


Fig. 3. Impedance (0.01Hz) over time of various acetic and phosphoric acid treated Mg alloy surfaces in 0.1 mol NaCl @ RT.

In addition, EIS was used to study the pre-treatment process. The impedance data from Figure 3 show higher values for samples treated with 100 g/L acetic acid than for all other samples. Especially for 300 g/L acetic acid one would expect the opposite result. In that case the removal of the huge amount of material may cause an increase of surface area which is not related to for the calculation of the impedance value by the software. The program uses a specific value that is given by the diameter of the area and not related to depth. For phosphoric acid the remaining phosphates may relativise the variations in concentration and treatment time. In general these results are more or less in the range of statistical variations of the alloy. Nevertheless, during 24h the impedance for the other samples increases with time. This might be explained by formation of a passive layer built from  $Mg(OH)_2$  additionally to the existing  $MgO$  that remains after the pickling at the surface of the samples. A passivation layer has to grow from the very beginning and does not exist during the first period of exposure. Based on these results a concentration of 100 g/L acetic acid with a treatment time of 60 s. at room temperature was chosen as pre-treatment of the Mg alloy for coating with the polymeric systems. The loss of material in an acetic acid concentration of 300 g/L was regarded as too high.

From literature polyetherimide (PEI) and different polyurethanes (PUR) are known as biocompatible and biodegradable in a certain manner [3, 6, 10]. Both polymeric systems offer a high variation for functionalization and intrinsic mechanical properties by only small changes in their chemistry. In general PURs contain different segments. They include nonpolar hard segments as well as polar soft segments derived from the chain extender and a diisocyanate. Therefore, microphase separation is possible which has consequences for the mechanical properties of the PURs[11]. Decreasing the molecular weight of the macrodiol and/or increasing the chain extender to diol ratio lead to harder and stiffer polyurethanes with higher tensile strength and lower elongation at break.

For coatings of the Mg alloy a 1K PUR and a 2K PUR were selected besides PEI. The 1K system was cross-linked by reaction of acrylic acid end groups while the 2K system consists of a

diol and a diisocyanate as hardener component that cross-linked the PUR by heat treatment. From Fig. 4 it is visible that the final coatings of PEI and the 1K PUR lead to porous polymeric layers while the 2K PUR system yielded a non-porous transparent layer. In all cases the thickness of the coating was between 5 and 10  $\mu\text{m}$  which, unfortunately, is not really ideal for comparison. Due to the different coating parameters for the systems a more equal thickness could not be realized in the frame of this work.

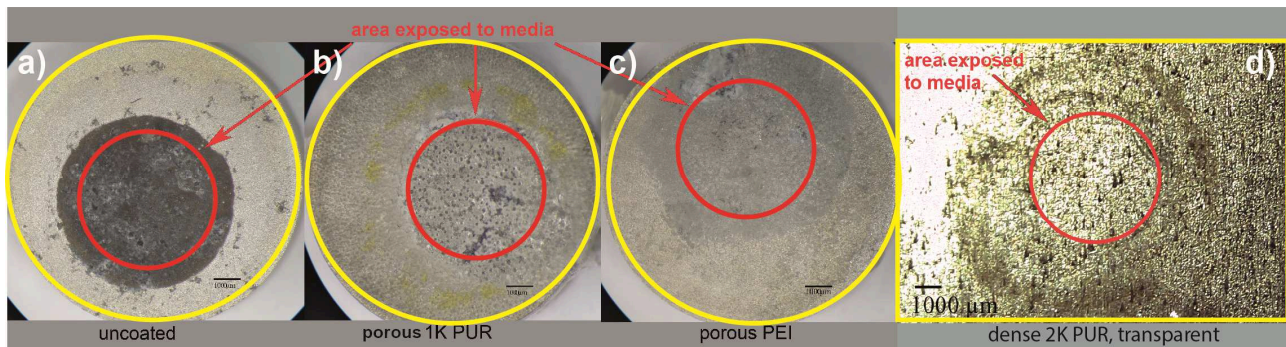


Fig. 4. Light microscopy photographs of uncoated (a) and two coated (porous 1K PUR (b) and porous PEI (c)) Mg alloy surfaces after exposure to HBSS for 1440 min @ 37°C; d) dense transparent 2K PUR after 1440 min in 0.1m NaCl @ RT; yellow area marks pre-treated respectively pre-treated and coated area.

During the preparation of the 1K PUR samples the growth of bubbles at the surface could be observed. Obviously, the acrylic acid reacted not only as a cross-linking system but also with the Mg alloy under formation of hydrogen (Fig. 4 (b)). From Fig. 5 it can be seen that during exposure to the electrolyte the impedance decreased by a factor of 5. Possibly these spongy areas break and electrolyte can directly contact the alloy surface to start a corrosive attack. The porous PEI coating did not cause hydrogen release while the 2K PUR builds a transparent and nearly perfect barrier layer. Evaluation of the impedance data from the EIS measurements in both media, 0.1 molar NaCl and HBSS, confirm this situation (because of the long duration the 2K PUR had only been investigated in NaCl. The impedance value did not change during another 6 weeks)

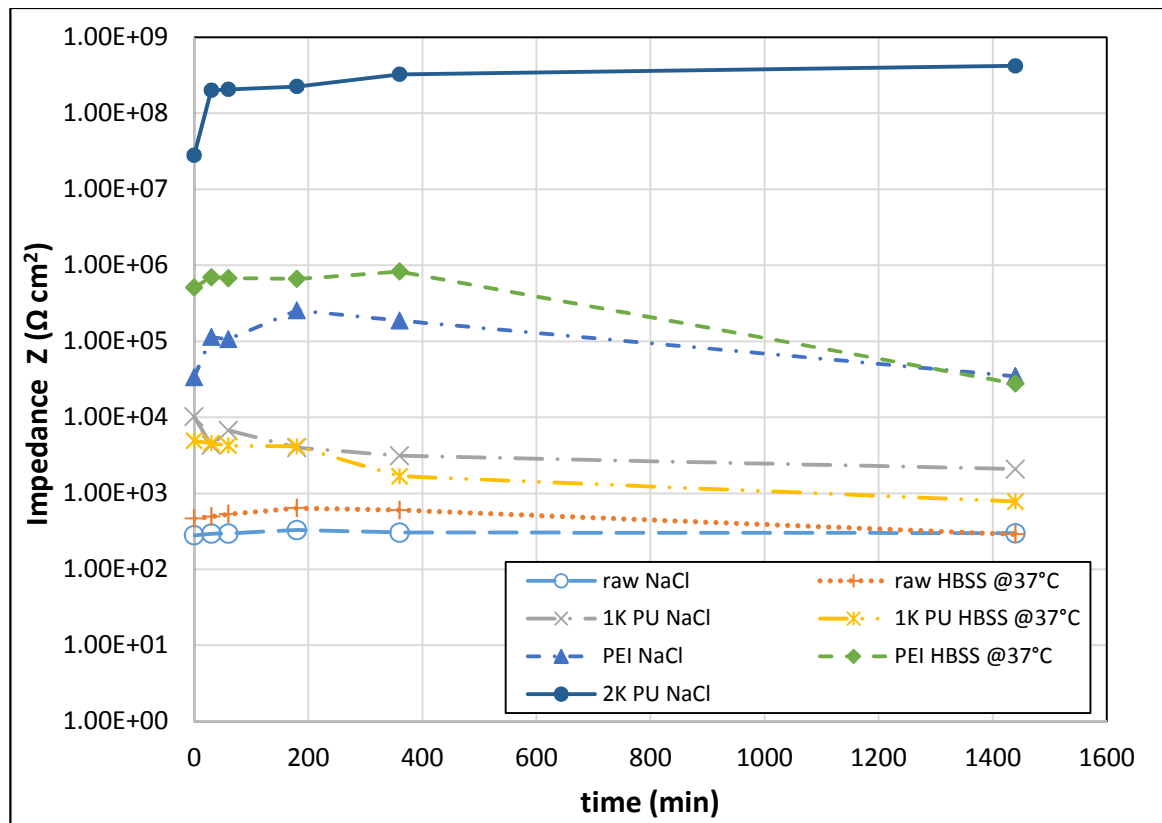


Fig. 5. Impedance (0.01Hz) over time for Mg alloy uncoated and with different types of polymeric coating

At the beginning of exposure the impedance values of the 1K PUR system are approx. 10 times higher than those of the uncoated sample while they decrease during time by a factor of 5 (see above). For PEI the barrier effect is 1 to 2 orders of magnitude higher than for the 1K PUR system. During the first 180 min swelling of the polymer coating occurs [10] (in case of NaCl) and increases the corrosion resistance by hindering the diffusion of the electrolyte. For HBSS the impedance value stays at a higher starting level which might be caused by the composition of the electrolyte, e.g. content and activity. However, after 24 hours for both media the impedance reached comparable values.

The situation for the 2K PUR is extremely different. The layer is non-porous and therefore the barrier properties prevent a corrosive attack from the electrolyte. The increase in impedance for the first 30 minutes might belong to a boundary layer caused by swelling of the polymer in the surface of the coating as the polymer chain includes some hydrophilic groups as in case of the PEI coating [4, 5]. This swelling additionally hinders the diffusion of ions from the electrolyte to the surface of the alloy. As the same in principle holds for HBSS, and due to the long stability of the coating, the 2K PUR was not investigated in EIS in this environment.

Nevertheless, the experiments demonstrate that the degradation behaviour of a Mg alloy coated with a polymer system can be influenced by the selection of the type of polymer and its intrinsic properties. Porosity also is an influencing parameter that helps to adjust the degradation rate in combination with the coating parameters and the thickness of the layer.

## Conclusions

The presented investigations and the resulting data demonstrate the importance of a pre-treatment as well as the selection of the coating polymer system for degradable implant materials. As some of the pre-treatment agents build specific layers on the surface of the alloy it probably influences the properties of the final coating, e.g. adhesion. Furthermore, the work shows that by selection of the appropriate type of polymer and its intrinsic properties the degradation rate of the system

coating/metal could be influenced. For PUR systems in general modifications in molecular weight, cross-linker, amount of hard and soft segments as well as network density influence the mechanical, barrier and degradation properties, e.g. a higher amount of carboxylic groups will decrease the lifetime of the coating by faster hydrolysis. The influence of the interface between pre-treated surface and polymeric coating will be a field of our investigations for the future.

## References

- [1] T.S.N. Sankara Narayanan, I.S. Park, and M.H. Lee, Strategies to improve the corrosion resistance of microarc oxidation (MAO) coated magnesium alloys for degradable implants: Prospects and challenges. *Progress in Materials Science* 60(0) (2014) 1-71.
- [2] K.K.L. Phua, E.R.H. Roberts, and K.W. Leong, Degradable Polymers, in *Comprehensive Biomaterials*, D. Editor-in-Chief: Paul, Editor. 2011, Elsevier: Oxford. 381-415.
- [3] A.T. Neffe et al., Controlled Change of Mechanical Properties during Hydrolytic Degradation of Polyester Urethane Networks. *Macromolecular Chemistry and Physics* 211(2) (2010) 182-194.
- [4] T.F. da Conceicao, et al., Corrosion protection of magnesium alloy AZ31 sheets by spin coating process with poly(ether imide) [PEI]. *Corrosion Science* 52(6) (2010) 2066-2079.
- [5] T.F. da Conceicao et al., Corrosion protection of magnesium AZ31 alloy using poly(ether imide) [PEI] coatings prepared by the dip coating method: Influence of solvent and substrate pre-treatment. *Corrosion Science* 53(1) (2011) 338-346.
- [6] M. Lange et al., Surface Functionalization of Poly(ether imide) with Linear, Methylated Oligoglycerols to Reduce Thrombogenicity. *Macromolecular Rapid Communications* 33(17) (2012) 1487-92.
- [7] J.H. Hanks. and R.E. Wallace, Relation of Oxygen and Temperature in the Preservation of Tissues by Refrigeration. *Proc. Soc. Exp. Biol. Med.* 71 (1949) 196.
- [8] U. C. Nwaogu et al., Influence of inorganic acid pickling on the corrosion resistance of magnesium alloy AZ31 sheet. *Corrosion Science* 51(11) (2009) 2544-2556.
- [9] U.C. Nwaogu et al., Effects of organic acid pickling on the corrosion resistance of magnesium alloy AZ31 sheet. *Corrosion Science* 52(6) (2010) 2143-2154.
- [10] N. Scharnagl, C. Blawert, and W. Dietzel, Corrosion protection of magnesium alloy AZ31 by coating with poly(ether imides) (PEI). *Surface and Coatings Technology* 203(10-11) (2009) 1423-1428.
- [11] C.J. Spaans et al., High molecular weight polyurethanes and a polyurethane urea based on 1,4-butanediisocyanate. *Polymer Bulletin* 41(2) (1998) 131-138.