Mechanical and corrosion properties of Mg-Zn/HAP/Al₂O₃ hybrid composite

F N Ahmad¹,² *, N Rashid³ and H Zuhailawati³

¹Faculty of Mechanical Engineering, Universiti Teknologi MARA, Cawangan Pulau Pinang, Jalan Permatang Pauh, 13500 Permatang Pauh, Pulau Pinang, Malaysia
²Biomaterials Niche Area, School of Materials and Mineral Resources Engineering, Universiti Sains Malaysia, Engineering Campus, 14300 Nibong Tebal, Penang, Malaysia
³*farra728@ppinang.uitm.edu.my

Abstract. The effect of HAP and Al₂O₃ composition with constant of ceramic content of 15 wt. % on mechanical properties, microstructure, and corrosion behavior of degradable Mg-Zn/HAP/Al₂O₃ hybrid composite developed by powder metallurgy method were investigated. The microstructure was analyzed using an optical microscope and scanning electronic microscope while mechanical properties were evaluated for density and compression strength. Meanwhile, corrosion behavior in Hank Balanced salt solution (HBSS) was studied for 4 h. The addition of HAP and Al₂O₃ particles has improved the mechanical properties and corrosion properties of Mg-Zn alloy. The results show that 15 wt. % Al₂O₃ (without HAP) shows the higher density, hardness, and compression. However, the composite consisted of 10 wt. % HAP with 5 wt. % Al₂O₃ shows the lower corrosion rate.

1. Introduction
Magnesium (Mg) and its alloy as potential attention in recent years for biomedical applications such as used in orthopedic implants owing to their excellent mechanical properties such as close to human bone, low density, light weight and excellent biocompatibility. The elastic modulus and density of Mg are about (41-45GPa, 1.74-2.00g/cm³) are closer to natural bone (1.8-2.1g/cm³, 15-20GPa) compared to stainless steel and titanium alloy[1]. Besides that, Mg is one of the most abundant metallic elements in the human body that is crucial to health and Mg²⁺ is able to be excreted by the kidneys [2]. However, the used of Mg is very restricted owing to their rapid corrosion in hydrogen release or degraded in Cl⁻ containing solution which reduces the mechanical integrity of Mg before the host tissues is sufficiently healed [3-4]. In an effort to solve the problem mentioned above, corrosion resistance can be improved in various ways such as surface treatment, coating, and alloying elements [5]. The addition of Zn (zinc) element content is less than 6 wt. % into Mg matrix can increase the strength, improve corrosion resistance and also can enhance the plasticity [6]. Zn also was added into Mg matrix can improve the mechanical and corrosion properties. Furthermore, the Mg-Zn alloys are biodegradable and can use as implant materials [7].

In recent years, many researchers have studied about combining the two reinforcement become hybrids composite to improve the mechanical and corrosion properties. Bioceramics have excellent osteoconductivity and corrosion resistance but the problem is they are very brittle and therefore cannot
be used as implant material alone or in single and the combination of metals and ceramic forming composite and hybrid composite can improve the both mechanical and corrosion properties [8]. One of these bioceramics, as hydroxyapatite (HAP) has a similar chemical composition and is biocompatible, non-toxic and osteoconductive [9].

On the other hand, alumina (Al₂O₃) has excellent corrosion resistance, biocompatibility, wear resistance and high hardness. The excellent properties can be used as reinforcement in Mg matrix. Al₂O₃ is bioinert and its corrosion resistance is very high (rate of corrosion 10⁻⁴ g.cm⁻²/day owing to a maximum corrosion rate of 1 mm in 10 years) [10]. Bioinert are implanted which were remains in human body as long as needed and sometimes forever so they can be removed by a second surgery.

Lately, the usage of powder metallurgy with mechanical alloying to synthesize Mg based alloys is a field of growing interest [11]. The advantage of using mechanical alloying (MA) compared to other technique is a solid state technique. Solid state technique is a technique that involves fracturing, re-welding and cold welding of blended powder in a high energy ball mill to produce a homogenous material. In this study, a metal matrix composite of magnesium as the matrix was added with zinc (Zn) as alloying element and HAP and Al₂O₃ particles as reinforcement have been investigated for mechanical and corrosive properties. So far, there are no reports on the addition of two reinforcement’s content such as HAP and Al₂O₃ into Mg-Zn alloy matrix forming hybrid composite. The aim of this paper is to discuss articles mechanical properties and corrosion behavior of hybrid composite of Mg-Zn alloy with a various compositions of HAP and Al₂O₃.

2. Experiments
In this study, Mg powder (99.00 % pure, <227.41μm), Zn powder (99.00% pure, <121.65μm), HAP and Al₂O₃ powder were refer to Mg-Zn/HAP/Al₂O₃ were mechanically milled with milling time 220 rpm for 1 hour. The composite Mg-Zn/HAP/Al₂O₃ with 0 wt. % HAP/15 wt. % Al₂O₃, 5 wt. % HAP/10 wt. % Al₂O₃, 10 wt. % HAP/5 wt. % Al₂O₃ and 15 wt. % HAP/5 wt. % Al₂O₃ respectively are known as 0 wt. % HAP, 5 wt. % HAP, 10 wt. % HAP and 15 wt. % HAP. Besides that, mechanical alloying was done using a high energy Fritsch Pulverisette P-5 planetary mill under argon gas atmosphere. Then, the powder to ball weight ratio of 1:8.75 was kept constant during the milling process using 20mm diameter stainless steel balls. Furthermore, the 3% n-heptane solution was added onto the powder mixture prior to the milling process to avoid excessive cold welding of the composite. The powders were pressed using compaction pressure 400MPa and thus were sintered at 300°C for an hour in argon flow. According to Archimedes principle density of the sintered alloy, the density was measured using pycnometer density equipment. The compression test was done by using a universal testing machine (UTM) Intron 5982. Meanwhile, for microstructure study, it was done by an optical microscope with magnification 50x. Then, for the corrosion test, the samples were immersed for 4h in Hanks Balanced Salt Solution (HBSS) bought from Sigma-Aldrich, St.Louis, USA. The usage of HBSS in this experiment because the HBSS contains all the physiological inorganic salt at a concentration that similar in the human body. Besides that, HBSS is the most usually used media in Mg in the previous literature. After that, the samples were put in a falcon tube that contains with HBSS solution and then immersed in a water bath with temperature 37°C for 4 h. The samples after immersed were washed with chromic acid solution and dried in the oven with temperature 70°C for 24 h and then tested for weight loss and microstructure analysis.

3. Results

3.1 Density and Compressive Strength
Figure 1 presents the result for density and compression for Mg-Zn/HAP/ Al₂O₃ hybrid composite. It can be noticed that the density and compression decrease with increasing HAP content. The increase in density and compressive strength for 0 wt. % HAP containing composite was due to the presence of the highest Al₂O₃ content (15 wt. % Al₂O₃) into the Mg-Zn alloy matrix. As known Al₂O₃ is hard
material and thus it can contribute to the increase in density and compressive strength. Meanwhile, for 15 wt. % HAP composite (which corresponds to the composition without Al₂O₃) was caused by two reasons. First, some degree of clustering of fine HAP particles takes place and second, the sintering temperature is insufficient for full densification. Previous research by Khalil et al. (2015) who was done researched by the addition of 10 wt. % of HAP into Mg-HAP and above gives a substantial drop in compressive strength value result due to the agglomeration of HAP particles [12]. Besides that, higher in HAP content will cause the value of compressive strength decrease due to its brittleness. Loy et al (2015) who worked on Mg-Zn/HAP composite discovered that the addition of higher HAP content can decrease the composite’s compressive strength [13].

Figure 1. Density and compressive strength of Mg-Zn/HAP/ Al₂O₃ hybrid composite.

3.2 Microstructure Observation
Figure 2 shows the optical microscope for Mg-Zn/HAP/Al₂O₃ with 0 wt. % HAP/15 wt. % Al₂O₃, 5 wt. % HAP/10 wt. % Al₂O₃, 10 wt. % HAP/5 wt. % Al₂O₃ and 15 wt. % HAP/5 wt. % Al₂O₃ respectively. As shown in the figure the present of porosity at 15 wt. % HAP is higher compared to the others composition. It shows that the presence of porosity can give influence to the resulted of mechanical properties as shown in the figure above with dropping the result of density and compressive strength. Besides that, it can be seen that the grain size of Mg-Zn matrix also decreases with increasing HAP content. It present that the addition of reinforcement content (HAP and Al₂O₃) can decrease the grain size of Mg-Zn/HAP/Al₂O₃ hybrid composite. Furthermore, the reducing in grain size in Mg matrix can significantly increase the mechanical properties and also can enhance the corrosion resistance.
Figure 2. Optical Microscope of hybrid composite with magnification 50x. 
(a) 0 wt. % HAP, (b) 5 wt. % HAP, (c) 10 wt. % HAP, and (d) 15 wt. % HAP.

3.3 Bio-corrosion Properties

Figure 3 shows the result of weight loss after immersion in HBSS for 4 h. Composite without HAP and with 15 wt. % HAP shows weight loss meanwhile for composite with 5 and 10 wt. % HAP show weight gain. The higher weight loss occurs for 0 wt. % HAP composite because no HAP is available that can promote apatite layer deposition on the composite surface. The corrosion ion attack at the pores occurred although the protection layer of apatite covers the surface. Weight gain is observed for 5 and 10 wt. % HAP containing composites was owing to the deposition of apatite on the whole surface composite and multiple protective from Mg(OH)₂ layer. Meanwhile, 15 wt. % HAP shows weight loss which is owing to the presence of higher porosity at the microstructure as shown in the optical micrograph. For 5 and 10 wt. % HAP composites show weight gain which is consistent with findings of Loy et al. (2016) who concluded the increment of HAP content exceeds 10 wt. % indicates the weight gain produced by apatite deposition layer surface on Mg-Zn/HAP composite.
Figure 3. The weight loss for Mg-Zn/HAP/Al₂O₃ composite after immersed in HBSS for 4 h.

Figure 4 presents the SEM image of the surface after immersion in HBSS for 4 h respectively. As seen in this figure, the 0 wt. % HAP content presents the considerable corrosion with cracks which lead to pitting and crevice corrosion thereby accelerating the weight loss of Mg matrix and also shows the present of needle in all surface that can slower the weight loss of corrosion [14-15].

Figure 4. The SEM image for Mg-Zn/HAP/Al₂O₃ composite with 0 wt. % HAP after immersed in HBSS for 4 h.

4. Conclusions
The influence of HAP and Al₂O₃ content on microstructure, mechanical and corrosion property of Mg-Zn/HAP/Al₂O₃ composite has been investigated. The main results can be summarized as follows such as the density and compression strength decrease with increasing HAP content. Meanwhile the grain size become refined with the addition of HAP and Al₂O₃ content. The addition of HAP can retard the composite from lost their weight in HBSS solution. Composite with 10 wt. % HAP (simultaneously has 5 wt.% Al₂O₃) provided the best result as biodegradable implant material with good density, compression and corrosion.
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