Properties of Porous Magnesium Using Polymethyl Methacrylate (PMMA) as a Space Holder

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Abstract. Porous magnesium has been recognized as a promising biodegradation metal for bone substitute application because of its excellent biocompatibility, low density, ability to biodegrade in vivo and excellent mechanical properties. In the present work, porous magnesium was fabricated by powder metallurgy using spherical polymethyl methacrylate (PMMA) as a space holder. To determine the optimum sintering temperature for porous magnesium fabrication, the porous magnesium was fabricated using double step sintering process at various sintering temperature (550°C, 585°C and 620°C) in first stage of research. The porous magnesium fabricated was then characterized for morphology, porosity, density and compressive strength. Density of porous magnesium increases and the porosity decreases with increasing sintering temperature. The mechanical characterization indicated that porous magnesium sintered at 620°C exhibited the highest compressive strength and density with optimum range of porosity of 39.37%. For second stage of research, porous magnesium with porosities of 39.38 – 40.82% was produced with different sizes of PMMA particles (38-63 µm, 63-90 µm and 90-125 µm). The compressive yield strength ranges between 19.95 MPa to 23.28 MPa and increases with decreasing PMMA particles size and porosity. These results proven that the PMMA has a potential to be used as space holder in porous magnesium for biomedical application.

1. Introduction
Magnesium has been recognized as a promising biodegradation metal especially for orthopedic applications. Comparing to other biomedical materials, they possess several advantages such as light weight, ability to degrade in vivo without any harmful effects and have elastic modulus which is closer to that of cortical bone. Currently, fabrication of magnesium with interconnected pores and suitable porosity is possible by using power metallurgy (PM) technique based on space holder particles. For this reason, space holder plays a very importance role in producing porous magnesium with desired porous architecture, mechanical properties and has no adverse effect on the resultant structure. Previously, Čapek and Vojtěch [1] synthesized porous magnesium using ammonium bicarbonate as space holder. They found that the total porosity of materials produced by powder metallurgy using the spacer particles is higher than the sum of the added ammonium bicarbonate. They also reported that the expansion of gases (NH₃, H₂O and CO₂) generated in the decomposition of ammonium bicarbonate could contribute to the increased in porosity. In addition, MgO was formed by the reaction of Mg and decomposed space-holding particles that containing oxygen [2]. It also have been reported that the residue of the decomposed space-
holding particles was found in the sintered porous Mg using ammonium bicarbonate [3] and carbamide [4] as space holders.

Any reaction between decomposed space-holding particles and magnesium framework may deteriorate the mechanical properties of the resulting scaffolds [5]. Hence, an alternative space holder materials with very worst affinity with Mg such as poly (methyl methacrylate) (PMMA) was utilised by Bi et. al [2]. Their study are focusing on the different percentage of PMMA but the effect of processing parameters such as sintering temperature and space holder sizes on porous structure and mechanical strength of porous were not detalles studied. Sintering temperature are important in determining the mechanical properties of porous magnesium as it governed the bonding between metal matrix particles in porous magnesium [5]. Moreover, compressibility of porous magnesium are mainly depending on the porosity and pore size [6].

In this work, PMMA space holder was used in fabrication of porous magnesium for biomedical purpose with the aim to reduce the undesired reaction between decomposed space-holder particles and magnesium matrix. At the same time, sizes of space holder and sintering parameter such temperature were studied to obtain an optimum parameter for fabrication of porous Mg. The pore morphology, pore size and distribution, total porosity and compressive strength of sintered porous magnesium were systematically discussed in this research.

2. Methodology

Porous magnesium was prepared by a powder metallurgical method using space holder technique. Pure Mg powder and PMMA particles were used as starting and space holder material respectively. The experiment was divided into two stages. In the first stage, the Mg powders were mixed with PMMA particles and with an Mg/PMMA weight ratio of 80:20. Then the powder mixtures were then compacted and heat treated using a two-step sintering process (550°C, 585°C and 620°C) under high purity argon atmosphere and tested for microstructure, density, porosity and compressive strength based . After obtaining optimum sintering temperature for fabricatio of porous Mg, the effect of pore size on the compressibility of porous magnesium were studied. Mg powders were mixed with three different sizes (38-63 µm, 63-90 µm and 90-125 µm) of PMMA particles and sintered with optimum parameter acquiring from the first stage. The sintered porous Mg were then characterized for density and compression test.

3. Results and Discussion

3.1 Microstructure Characterization of Porous Magnesium

The microstructure of porous Mg sintered at three different temperature is shown in Figure 1. The sintered porous Mg had an open-cell structure with uniform pore structure and were distributed homogeneously. This indicated that PMMA space holder and Mg powder produced a homogeneous mixture. The pores shape formed is not perfectly spherical shape. However, there is no significant differences in pore morphology noticed for all the sintered samples. There has two types of pores as shown in Figure 2. The first type of pore (indicated by yellow arrow) has irregular shape. This pore may formed due to expansion of trapped gas during sintering process and incomplete compaction during pressing [3]. The first type of pore also known as micro-pores. This type of pore will reduce the compressive strength of porous Mg due to decrement of load-bearing cross-section area of cell wall [7]. The second type pore (indicated by red arrow) are isolated from each other and have size larger than 100 µm, which is suitable for bone cell ingrowth [8]. There are most likely originated from the decomposition of PMMA particles. Čapek and Vojtěch [3] and Wen et al. [6] using ammonium bicarbonate and carbamide as space holder material have also claimed that two types of pores were formed during porous Mg fabrication. However, compared with other organic space holders such as carbamide and ammonium bicarbonate, PMMA is a polymer with very poor affinity with Mg [2]. As a result, a more uniform pore in the sintered Mg can be easily obtained using PMMA with almost perfectly spherical shape.
Figure 1. SEM micrograph of porous magnesium sintered at (a) 550°C (b) 585°C and (c) 620°C (→ pores)

Figure 2. SEM micrograph of porous magnesium sintered at (a) 550°C (b) 585°C and (c) 620°C (type I and II pores are indicated with arrow)

3.2 Sintered Density and Porosity of the Porous Magnesium

Figure 3 shows density and porosity versus sintering temperature. It can be seen that the porosity of porous Mg linearly decreases with increasing density and sintering temperatures. The figure also indicated that samples sintered at 620°C more compacted as compared to samples sintered at 550°C and 585°C. As the sintering temperature increases, the number of inter-particle contacts of Mg increases. This help to improve the growth of sintering necks that ultimately contribute to densification and the decrement of micro-pore sizes [7]. Since the porosity is inversely proportional to the measurement of bulk density, the porosity of porous Mg decreases as the density and sintering temperature increases. However, partial melting of matrix powder and evaporation of some alloying element may occur if the sintering temperature is too high as reported by Dewidar et al. [9]. The density and porosity achieved for the samples are closed to natural bones (density :1.8-2.1 g/cm³ and porosity :20-70%) [3, 10].

Figure 3. Density and porosity of porous magnesium versus sintering temperature
3.3 Compressive Behavior of Porous Magnesium

Figure 4a exhibits uniaxial compressive stress–strain curves of the porous magnesium sintered at different temperature. The result shows that all compressive stress–strain curves of porous Mg showed ductile behavior under compression and consist of three regions: linear elastic region, plateau region and the densification stage. When the load raised, the stress–strain curve switch from the linear elastic regime to the plateau regime. At plateau stage, the flow stress with some serrations become relatively consistent with the increasing strain. According to Hao et al. [11], present of serrated plateau was mainly due to repeated break and squeeze of the cell wall as the cell wall contain voids and interstices. In fact, the serrated plateau reveal the brittle deformation mode occurs at the cell walls after the yield. As the compression get going, collapse of the cell wall happened caused by rapid propagation of cracks. However, it was observed that porous Mg sintered at 620 °C exhibits different pattern of plateau curve as compared to samples sintered at 550 °C and 585 °C. It showed an increase in compressive strain with the increasing compressive stress, rather than a constant stress plateau. Plateau region are ended after all the voids and pores are virtually eliminated. At last stage, densification stage, it happened beyond 0.45 compressive strain for all sintered samples. The stress increases steeply with the strain increasing slightly due to rapid rise of the resistance of porous Mg as the Mg matrix start to be compressed. In general, the curves showed that the porous Mg that sintered at 620 °C yielded at a higher stress state than those sintered at 550 °C and 585 °C.

Compressive yield strength of the porous magnesium versus sintering temperature are display in Figure 4b. The result indicated that the compressive yield strength of the porous Mg increased with an increase in the sintering temperature. The average yield strength increase from 26.42 MPa to 28.93 MPa with the increasing of sintering temperature from 550 °C to 620 °C. This result can be explained by increase in the number of Mg inter-particle contact during solid state sintering as the sintering temperature increases [12]. In addition, reduction of micro-pores and densification could occur because of enhancement of growth of sintering necks. The yield strength was matched with the average density obtained in the density and porosity test. According to Gibson-Ashby theory, the most influential structural characteristic of porous metal affecting the mechanical properties is its relative density [12]. For this reason, the yield strength of porous Mg increases with the decreasing of total porosity. However, Arifvianto and Zhou [5] have revealed that sintering temperature must not be too high as it could lead to partial melting that influenced resulting pore shape and pore sizes. Overall, the yield strength values of porous Mg are fall within the range of cancellous bone [3]. However, the porosity the porosity range should be take into account since a suitable range of porosity is crucial for bone substitute application.
Among the porous magnesium samples, the sample sintered at 620°C exhibited the highest compressive yield strength and density with optimum range of porosity at around 39.37%. Hence, sintering temperature of 620°C was used on the second stage of experiment, to study the effect of different sizes of space holder on density, porosity and compressive properties.

### 3.4 Sintered Density and Porosity of the Porous Magnesium with Various PMMA particle sizes

The result of density and porosity of porous magnesium prepared with various size of PMMA particles is shown in Table 1. The average density of sintered porous Mg prepared with 38-63 µm, 63-90 µm and 90-125 µm of PMMA are 1.058 g/cm³, 1.043 g/cm³ and 1.030 g/cm³ respectively. The porosity slightly increased from 39.38 % to 40.82 % with increasing particle size of space holder particle, although identical weight ratio of Mg/PMMA was used for all samples. Also, it is noted that the total porosity of all porous Mg samples was higher than the sum of the added PMMA. The main reason of deviation of total porosity from designed values was due to present of micro-pores. Since the total porosity of the porous Mg is calculated from the sum of macro-porosity and micro-porosity, therefore the total porosity greater than designated value.

#### Table 1. Density and porosity of porous magnesium prepared with various size of PMMA particles

| Particle Size (µm) | Density (g/cm³) | Average Density (g/cm³) | Porosity (%) | Average Porosity |
|-------------------|----------------|-------------------------|--------------|-----------------|
| 38-63             | 1.058          | 1.058                   | 39.20        | 39.38           |
|                   | 1.062          |                         | 38.97        |                 |
|                   | 1.055          |                         | 39.37        |                 |
| 63-90             | 1.044          | 1.043                   | 40.00        | 40.06           |
|                   | 1.040          |                         | 40.23        |                 |
|                   | 1.045          |                         | 39.94        |                 |
| 90-125            | 1.017          | 1.030                   | 41.55        | 40.82           |
|                   | 1.037          |                         | 40.40        |                 |
|                   | 1.035          |                         | 40.52        |                 |

#### 3.5 Compressive Behavior of Porous Magnesium with various size of PMMA particles

The stress-strain curve of porous magnesium prepared with different size of space holder is shown in Figure 5 and Table 2 summarized the values of compressive strength for all the samples. In all cases, the stresses strain curves consist of three distinct zones, i) elastic deformation zone (0-0.2 of strain) where stress and strain increases linearly until yield point ii) plateau zone (0.2-0.8 of strain) where serration of flow stress occurs and iii) densification zone (>0.8 of strain) where the limit stress rapidly increases. It was observed that porous Mg prepared with 38-63 µm yield at a higher stress than those with 63-90 µm and 90-125 µm. The decreasing trend in yield strength for porous Mg containing 63-90 µm and 90-125 µm PMMA particles are correlated with the increasing of porosity. The sizes of space holder have a great influenced on the cell wall. Larger particles size of space holder formed thinner cell wall thus not enough to support the load during compressive test. As a result, the failure of porous Mg prepared with 90-125 µm occurs at relative lower stress compared to others. Moreover, interconnected pores that act as crack initiation might present in porous Mg with higher porosity and causing the stress easily propagate through the framework of samples [13]. Gibson and Ashby revealed that the collapse stress of porous metal is not affected by the pore size [6]. However, the results in the present analysis showed that compressive strength increased with decrease in pore size. Also, it is necessary to determine the upper limit in pore size as bigger pores size could compromise the mechanical properties of porous Mg through increases in void volume. In general, the mechanical properties of the porous Mg fall within the range of those of cancellous bone (2-180 MPa). For that reason, it is proven porous magnesium with PMMA as a space holder is one of the potential candidates for biomedical application especially for hard tissue generation.
Figure 5. Stress–strain curves of porous magnesium prepared with (a) 38-63µm (b) 60-125 µm and (c) 90-125 µm of PMMA particle

Table 2. Compressive yield strength of porous magnesium prepared with various size of PMMA

| Particle Size of PMMA (µm) | Compressive Yield Strength (MPa) | Average (MPa) |
|----------------------------|---------------------------------|---------------|
| 36-63                      | 24.45                           | 23.28         |
|                            | 22.89                           |               |
|                            | 22.50                           |               |
| 63-90                      | 21.38                           | 21.62         |
|                            | 22.54                           |               |
|                            | 20.95                           |               |
| 90-125                     | 18.14                           | 19.95         |
|                            | 19.07                           |               |
|                            | 22.63                           |               |

4. Conclusion
Porous magnesium with PMMA space holder was successfully prepared by powder metallurgy method using space holder technique. The compressive yield strength ranges between 19.95 MPa and 23.28 MPa and increases with decreasing PMMA particles size and porosity. The mechanical properties of porous Mg produced is in the range of compressive strength of natural bone

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