DEVELOPMENT OF CRANIOFACIAL IMPLANTS PRODUCED BY METAL INJECTION MOLDING OF TITANIUM ALLOY USING NOVEL BINDER SYSTEM BASED ON PALM OIL

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Abstract. Metal Injection Molding (MIM) is a cost-effective technique for producing small, complex, precision parts in high volumes. MIM consists of four main processing steps: mixing, injection molding, debinding and sintering. In the mixing step, the powder titanium alloy (Ti6Al4V) medical grade is mixed with a binder system based on palm stearin to form a homogeneous feedstock. The rheological studies of the feedstock have been determined properly in order to success during injection into injection molding machine. After molding, the binder holds the particles in place. The binder systems then have to be removed completely through debinding step. Any contamination of the binder systems will affect the final properties of the parts. During debinding step, solvent extraction debinding has been used to remove partly of the binder systems. The debound part is then sintered at high temperature under control atmosphere furnace. The properties of the sintered craniofacial implants then was measured and compared. The sintered craniofacial implants also then were determined in term of in-vitro cytotoxicity study using mouse fibroblast lines L-929. The results show that the sintered craniofacial implants of titanium alloy produced by MIM fullfill the in-vitro cytotoxicity test.

Introduction

Titanium and its alloys have become very popular materials because of their low density, high corrosion resistance and excellent mechanical properties [1,2]. Today also the usefulness of titanium in medical implants, for exclusive sporting gears and also for jewelry is recognized. Titanium parts are still expensive not only because of high raw materials prices but also because of difficulty forming, machining and welding. This is why the near net shape forming of titanium is very advantageous. Metal injection molding (MIM) as a near net shape process for high production number of small intricate parts is a desirable alternative [3].

In the MIM process, the binder is a key component, which provides the powder with the flowability and formability necessary for molding even though it is temporary. The binder systems that commonly used for injection molding technique were based on thermoplastic materials. In this study, the palm oil derivative which is palm stearin has been formulated and evaluated as a possible alternative binder system. The reason for using palm stearin as a binder system is due to its contents that can be advantages during debinding process. It is important that the removal of binder be performed gradually to maintain the shape of the debound part. At different heating temperature, the binder melts leaving different impurities at different melting point. The remaining impurities help forming capillary holes for the removal of the rest of the binder material [4,5]. Therefore, the selection of palm stearin as a possible alternative binder system fulfills the important criteria of a binder system in PIM process as its components exhibit various melting points.

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Experimental Procedure

The morphology of the titanium alloy powder medical grade is shown in Fig. 1. It shows that the particle shape of the powder is spherical. This leads to an optimum powder loading in the feedstock between 65 to 67 volume percent and it is possible to make a good moldings. The mean size of the titanium alloy powder medical grade is 25 µm were used in the investigation.

![Fig. 1: The Morphology of the Titanium Alloy Powder Medical Grade.](image)

Combination of polyethylene and palm stearin was used as the binder system. The binder system comprised 40% of polyethylene and 60% of palm stearin (percentage by weight). The powder was mixed with the binder system at the temperature range of 130 to 160°C for 2 hour using z-blade mixer. The feedstock then was studied in term of rheological which is the viscosity and shear rate were measured using Capillary Rheometer. The Vertical Injection Molding Machine was adopted to mold into the tensile strength test part. The green molded parts were subjected to a solvent extraction step where two third of the binder system was removed. The green molded parts then were immersed into the heptane for 6 hours at the temperature of 60°C. The part then was continued heated at 10°C/min up to 1150°C under vacuum atmosphere with holding time of 4 hours using High Temperature Control Atmosphere Furnace. Fig. 2 shows the schematic process of Metal Injection Molding (MIM) technique.

The density of each of the sintered part was measured using Densimeter ED-120T. The hardness of the each sintered part was measured using Vickers Hardness Tester. The ultimate tensile strength of the sintered part was measured by Instron Universal Tensile Strength Machine. The phase diagram of the sintered specimen was measured using X-Ray Diffraction Spectroscopy (XRD). Optical Micrograph was used to observe the microstructure of sintered part. The carbon content of the sintered part was determined using Carbon Analyzer LECO CS-244. The in-vitro cytotoxicity assay was tested on the extraction of the part using mouse fibroblast cell lines L-929 by means of CellTiter96® AQUEOUS One Solution Cell Prolifiration (MTS) assays. Meanwhile, the in-vitro cytotoxicity assay on the direct contact was observed using Scanning Electron Microscopy (SEM) using mouse fibroblast cell lines L-929 was measured after 72 hours of incubation [6,7,8].
Fig. 2 shows the schematic process of Metal Injection Molding (MIM) technique.

Results and Discussion

Rheological Study of Titanium Alloy

Fig. 3 shows the viscosity versus shear rate at different temperature of titanium alloy feedstock. The graph indicated clearly that as the viscosity decrease the shear rate increase relatively to the increasing of the temperature.

The results conclude that the viscosity of the feedstock exhibit pseudo-plastic behavior, which is common for MIM feedstock. The variation of viscosity versus shear rate in log-log scale graph is almost linear, which is an indicator of feedstock stability. In order to inject the feedstock into injection molding machine, the shear rate and viscosity should be in the range of 100s$^{-1}$ to 10000s$^{-1}$ and 1000Pa s respectively. The recommended temperature range that can be injected for the titanium alloy feedstock is 110$^\circ$C to 140$^\circ$C. Pseudo-plastic fluid of the feedstock also indicates the decreasing of viscosity with increase shear rate and temperature. At low temperature the feedstock viscosity is too high for standard molding conditions, while at high temperature results in binder separation that leads to defect of the injected parts.

Fig. 3 shows the viscosity versus shear rate at different temperature of titanium alloy.
Physical and Mechanical Properties
The physical and mechanical properties of the sintered titanium alloy parts were shown in Table I. The results show that the sintered titanium alloy parts have achieved the minimum requirement for sintered MIM parts compared with Standard Metal Powder Industries Federation (MPIF) 35 for the sintered titanium alloy except for elongation. Microstructure observation using optical micrograph clearly shows the crystalline pattern occurred on the sintered titanium alloy parts. The structure also clearly shows the formation of beta (β) grain and alpha/beta (α/β) lamellae structure of sintered titanium alloy and it is shown in the Fig. 4 (a). Fig. 4(b) show the XRD results on the sintered titanium alloy part showing the formation of TiC (titanium carbide) phase which will be affected on the ductility of the sintered titanium alloy parts. The result for the carbon contents is shown in the Table II. It shows that the increasing of carbon content from 0.08% to 0.33%. The increasing of 0.28% probably due to the contamination of the binder system that still remains in the sintered titanium alloy parts. This may cause the brittleness of the sintered parts of titanium alloy.

Table I: The Physical and Mechanical Properties of the Sintered Titanium Alloy Part.

| Properties      | Sintered Titanium Alloy | MPIF 35 |
|-----------------|-------------------------|---------|
| Density (g/cm³) | 4.38                    | > 96 %  |
| Hardness (Hv)  | 335.00                  | 300-400 |
| Porosity (%)    | 2.62                    | < 5     |
| Shrinkage (%)   | 11.92                   | 12 - 15 |
| Strength (MPa)  | 830.00                  | > 700   |
| Elongation (%)  | 1.74                    | 10-15   |

Fig. 4: The Micrograph Observation (a) and XRD results (b) of the Sintered Titanium Alloy Part.

Table II: The Carbon Contents of the Sintered Titanium Alloy Part.

| Carbon Content (%) | Titanium Alloy Powder | Sintered Parts |
|--------------------|-----------------------|---------------|

In-Vitro Cytotoxicity Study
The in-vitro cytotoxicity study of titanium alloy part produced by MIM technique was evaluated on mouse fibroblast L929 cell lines. The results on the CellTiter 96® AQUEOUS One Solution Cell Proliferation assays (MTS) were depicted in Fig. 6. The percentage of viable cells compared to
control values obtained from titanium alloy part extract for cytotoxic assays results in a significantly higher values ($p<0.05$) with respect to 0.1% phenol (positive control) and comparable to the vehicle control (negative control). These results indicate that the titanium alloy part is non toxic to mouse fibroblast cell lines L-929.

The growth of mouse fibroblast cell lines L-929 on the surface of titanium alloy part for 72h were shown in Fig. 7. Most of the cells were attached to the titanium alloy part and proliferated with numerous filopodia. The morphology on the surface also showed the rounded cells indicating that the cells in mitosis.

![CellTiter 96® Aqueous One Solution Cell Proliferation Assay](image)

**Fig. 6:** The Percentage (%) of Viable Cells Compared to Control on the Titanium Alloy Specimen.

![filopodia](image)

**Fig. 7:** The Growth of Mouse Fibroblast Cell Lines L-929 on the Surface of Titanium Alloy Part for 72h Incubation.

**Conclusion**

The feedstock of using palm stearin as a noval binder system is suitable for injection molding machine with the shear rate and viscosity of the feedstock is in the range of $100s^{-1}$ to $10000s^{-1}$ and 1000 Pa s respectively. The properties of the sintered titanium alloy part have achieved the minimum requirement for sintered MIM parts compared with the Standard Metal Powder Industries Federation (MPIF) 35 for titanium alloy part except for the elongation due to the formation of TiC. The crystallinity structure of titanium alloy was shown clearly on the micrograph. The in-vitro cytotoxicity assay results indicate that the titanium alloy part is non toxic to mouse fibroblast cell lines L-929.
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