Thermal pyrolysis optimization for highest density of Ti-6Al-4V mix with Palm Stearin and Polyethylene

N H Mohamad Nor1,*, N Muhamad2, H Husain1, S Shawal1, M S Moon1, M Fauzi1, Muhammad Fairuz Remeli1 and J B Saedon1

1 Faculty of Mechanical Engineering, Universiti Teknologi Mara (UiTM), 40450 Shah Alam, Selangor, Malaysia
2 Dept. of Mechanical and Materials Engineering, Faculty of Engineering & Built Environment, Universiti Kebangsaan Malaysia (UKM), 43600 Bangi, Selangor, Malaysia

*Corresponding author: norhafiez@uitm.edu.my

Abstract. Titanium metal injection molding (Ti-MIM) is coming ever closer to delivering its promise of high value markets, such as the aerospace and medical sectors. It is therefore an inspiration in this study to try to use palm stearin (PS) combined with backbone polyethylene (PE) for injection along with Ti-6Al-4V atomized powder. The uniqueness of PS is a potential binder system that can be used since it is very cheap material and highly available in Malaysia. The present work attempts to optimize the process parameters of thermal pyrolysis stage using Taguchi method of orthogonal array. Density is important characteristic in determine the quality of the brown part. Using these characteristics, the heating rate, temperature and soaking time are optimized in this study. The results show that no swelling or distortion was observed on the molded specimens on both binder systems. It was found that heating rate was the most significant factor followed by pyrolysis time and pyrolysis temperature. A verification test was also performed to prove the effectiveness of Taguchi technique after all the optimum parameters were determined. The optimization of thermal pyrolysis prepared in this study has enabled to improve the final density and mechanical properties of final part. Based on these results, sample displaying yield strength of 929.91 MPa and a plastic elongation of more than 12.15% were produced and meet the requirements of the ASTM B817-08.

Keywords. Taguchi method; Metal injection molding (MIM); Brown part; Ti-6Al-4V; Palm stearin; Thermal pyrolysis.

1. Introduction
Metal injection molding (MIM) has gotten an increasing attention as a low-cost production technique for small, precise and intricate part made in high volumes [1]. The technique involves mixing of the metal powder with a binder, injection of the feedstock into a mold, removal of the binder and then sintering as the last step to consolidate the product to its final density [2]. Recently, metal injection molding of Titanium (Ti-MIM) has a promising demand from the market especially in aerospace and biomedical field. Formulation of a binder system has a substantial influence on the success of MIM production [3].

Selection of binder system in production of Ti-MIM can affect the presence of other elements to react on an as-sintered product rather than the condition during the experiment [4]. Titanium is a very
reactive metal that can interact with other elements and easily cause oxidation to be occurred [5].

The oxidation on as-sintered product can lead to deficiency of its physical and mechanical strength.

Numerous researches has been made in order to analyze the effect on different binder system in the process of Ti-MIM as Dehghan-Manshadi [6] reported that titanium reacts strongly with oxygen, nitrogen, carbon and hydrogen. Reference [4] also reported that high levels of oxygen are often found in inexpensive titanium powder sources.

In this study, injected Ti-6Al-4V feedstock that consists of PS and PE as the binder was used to investigate the optimization of pyrolysis parameters for PE removal from the brown part in thermal pyrolysis process. Palm Stearin (PS) binder is a binder system to substitute with multi-components conventional binder system and Malaysia has abundant resources of PS [7]. Thermal pyrolysis process is crucial to determine the success of an as-sintered product [3]. Firstly, the injected sample or green part was soaked into heptane for solvent pyrolysis to remove PS followed by removal of PE through thermal pyrolysis process. Highest density of brown part sample after removal of PE has been recognized as an output for this study.

Taguchi method is an alternative approach in Design of Experiment (DOE) technique that uses orthogonal array as a basis of experiment in order to optimize the productivity [8]. The advantage of using Taguchi’s approach is fewer experiments can be conducted involving many processing parameters that can affect the final results of the process. It is very efficient, simple, cost-effective and time saving approach. As reported previously from Mohamad Nor et al. [9], 5 °C/min of heating rate for 60 minutes of heating time was enough to eliminate PE from Ti-6Al-4V brown part. Therefore, based on Mohamad Nor et al. [9] three factors that have big influence on thermal pyrolysis were chosen in this study which are: heating rate; temperature of thermal pyrolysis and time of heating. Each factor has three levels to be optimized and expressed in term of S/N ratio in order to identify which of them is the best set of parameter. Then, analysis of variance (ANOVA) was applied on the best set parameter to find a factor that gives the utmost contribution which affects the quality characteristics [10].

Additionally, the ANOVA was also used to validate the results from the optimized parameters by replicating the thermal pyrolysis process. The brown part sample then analyzed under SEM after thermal pyrolysis process to assure the absence of PE or other elements especially oxygen and carbon that can easily react with Titanium.

2. Experimental procedure

2.1. Materials

The binder materials used in this study consists of PS acting as primary binder while LDPE is the backbone or secondary binder. The density of PS was 0.891g/cm3 while LDPE density was 0.91 g/cm3. The composition of binder used in this study was 60wt% PS and 40wt% LDPE. This composition was chosen because it was stable based on a studies by Ismail et al. [11], Omar et al. [12] and Subuki et al. [13] which applies the binder material to a spherical-shaped 316L stainless steel powder. The Ti-6Al-4V metal powder used in this study is a spherical shape with 18.8 μm average size produced through the gas atomizing. Table 1 presents the characteristics of the Ti-6Al-4V metal powder used in this study while Table 2 presents its chemical content. Figure 1 shows the scanning electron microscope (SEM) of Ti-6Al-4V powders which are spherical in shape.

| Table 1. Ti-6Al-4V powder physical properties. |
|------------------------------------------------|
| Particle size distribution (μm) | Pycnomete density (g/cm³) | Melting Temperature (°C) |
| D₁₀ | D₅₀ | D₉₀ |
| 11.2 | 18.8 | 30.5 | 4.38 | 1650 |
Table 2. Chemical composition of Ti-6Al-4V powder.

| Al  | V   | C   | Fe  | O   | N   | H   | Ti (wt%) |
|-----|-----|-----|-----|-----|-----|-----|----------|
| 5.99| 4.08| 0.005| 0.043| 0.185| 0.004| 0.002| Bal      |

Figure 1. SEM image of Ti-6Al-4V powder.

2.2. Mixing
The binder was heated at 150°C in the sigma-blade mixer. In this temperature LDPE was totally melted and in mixing with PS which was a viscous colloidal gel, provided a suitable condition for being blended with Ti-6Al-4V powder. Then Ti-6Al-4V powder was gradually added to achieve a feedstock with 65vol% powder loading. The mixing procedure continued for 60 min to ensure a homogeneous feedstock. After mixing, the feedstocks were crushed to form in granule form.

2.3. Injection molding
Feedstock injection molded was performed using a Battenfeld injection molding machine BA 250/50 CDC. Figure 2 shows the schematic diagram of the tensile bar cavity. The feedstock provided was injected through a mold that produces a specimen for the tensile test. Proper temperature settings (100–200 °C), pressure (0.1–130 MPa) and velocity of rotation of the screw (35–70 rpm) should be used for injection molding as referred to by German [3]. The green parts should be easily released through the die after injection molding and be sufficiently hard to be ejected without failure. In addition, the green parts produced must be free of defects.

Figure 2. Dimension (mm) of tensile bar cavity with thickness of 3.17 mm.

2.4. Thermal pyrolysis
Prior to the thermal pyrolysis, the PS binder was removed by soaking the green part sample in heptane solution for 6 hours. At this stage it is called brown part but PE binders still remain bonded and covered the Ti-6Al-4V powder. Figure 3 presents SEM image of brown part after soaking in heptane. It can be seen the backbone of PE binder still remains to bind the particle powders and to retain the shape. The removal of PE binder process was then continued by thermal pyrolysis process. In this study, second stage of debinding (thermal debinding) and sintering process were conducted in a VTC-500 4TSF VAC-TEC vacuum furnace. Samples were placed in furnace and temperature was gradually increased to 500 °C to remove residual binder (LLDPE). Samples were kept at this temperature for 1
h, then temperature was increased to 1300°C with the rate of 5 °C/min. The temperature schedule applied for sintering is given in figure 4.

![Figure 3. SEM image of brown part after soaking in heptane for 6 hours.](image)

![Figure 4. Thermal debinding and sintering cycle used for tensile bar test specimens.](image)

2.5. Design of experiment
With an appropriate DOE, one can quickly and with fewer number of trials, it is important to find out whether the variables have an effect on the output quality. In this experiment, Taguchi’s method of \( L_9^{(3^4)} \) orthogonal array was used which make a fewer attempts comprising 9 tests compared to conventional “trial and error” test which can make up to 81 tests. From Taguchi’s method it can be able to identify which parameters that contributed the most to produce highest density after the removal of PE. The chosen parameters are based on the TGA results from the characterization of PE binder that has studied previously by Jamaludin et al. [14] as shown in table 3.

| Table 3. Parameter design of experiment. |
|-----------------------------------------|
| Factors                  | Level |
|--------------------------|-------|
| Heating Rate (°C/min)    | 4 5 6 |
| Pyrolysis Temperature    | 505 510 515 |
| Soaking Time             | 90 120 150 |
2.6. ANOVA and confirmation experiment
After the best set of parameter obtained from Taguchi’s method, the analysis of variance (ANOVA) was applied to find the relationship in which parameter contribute the most affecting quality characteristic. From the results, a confirmation experiment was conducted to verify the optimal parameters processing obtain from the designed parameters. After the confirmation has been done the brown part was examined under SEM to observe the presence of other contamination. In addition, sintering process was conducted to strengthen the confirmation result and to ensure the success of the MIM process.

3. Result and discussions
3.1. Injection moulding
Figure 5 shows green part of 65vol% has been produced by injection process. SEM image shows homogeneous of green part have been produced where no powder-binder separation occurred. Nevertheless, the injection process went smoothly and there were no defects were observed such as short shot, crack and sink mark. The optimum temperature and pressure set for injection molding was 450 bar and 140°C respectively. Green parts consist of adequate stiffness and mechanical strength of samples were evaluated by the triple point bending test.

![Figure 5. Green part of 65vol% injected with no powder-binder separation defect.](image)

Figure 6 shows the physical differences between the green part, the brown part after solvent pyrolysis and the brown part after thermal pyrolysis. Only colour changes in the sample occurred due to the small shrinkage occurring on the brown part. About 94%–98% of LDPE was removed during thermal pyrolysis for almost 4.6 hours in vacuum furnace. The remaining binder of LDPE was used to sustain the shape of brown part prior to sintering. At this stage, the brown part is very fragile since it has no bound between particles. In both binder systems, the entire pyrolysis cycle is about 10 h in duration which represents a considerable shortening compared to the conventional process of thermal degradation. In addition, it is possible to eliminate the hazardous solvent during pyrolysis with the PS/LDPE binder system and in practice it is very safe and cheap.
Figure 6. The difference between a) green part, b) brown part after solvent pyrolysis, and c) brown part after thermal pyrolysis.

Figure 7 presents morphology of a brown part sample that shows PE binder has been removed completely. However, there was one thin layer of PE binder between the powder particles to bind the Ti-6Al-4V powder together for sintering process. Formation of variable size of pores was presence in the brown part sample after thermal pyrolysis process. At this state, brown part sample was very brittle because no more bond among Ti-6Al-4V powder particles. Pore structures will be ruptured after the brown part is sintered and the density of the sample will increase as well as the sample strength.

3.2. Injection moulding

In order to gain optimal performance of the removal of PE from the brown part part, the S/N ratio of the larger-the-better was used for the experiment which the formula is defined as:

$$\frac{S}{N} = -10 \log \left( \frac{1}{n} \sum_{j=1}^{n} \left( \frac{1}{Y_{ij}} \right) \right)$$  \hspace{1cm} (1)

Where \( n \) is the total number of shots for each trial and \( Y_{ij} \) is the amount of score for the brown part density. Table 4 shows orthogonal array with calculation of S/N ratio. T value is the mean of total S/N ratio which then will be used to compute the optimum range performance.
Table 4. Orthogonal array with S/N ratio for brown density.

| Test | Parameter | Density of Brown Part | S/N |
|------|-----------|------------------------|-----|
| 1    | A0 B0 C0  | 2.8979 2.9266 2.9987  | 9.36741 |
| 2    | A1 B1 C1  | 2.9236 2.8957 2.9369  | 9.30344 |
| 3    | A2 B2 C2  | 2.9075 2.9063 2.9178  | 9.27941 |
| 4    | A0 B0 C1  | 2.9093 2.9169 2.9397  | 9.31325 |
| 5    | A1 B1 C0  | 2.9625 3.1108 2.9691  | 9.57668 |
| 6    | A2 B2 C1  | 2.9757 2.9068 2.9157  | 9.04736 |
| 7    | A1 B0 C2  | 2.9024 2.9028 2.9008  | 9.25395 |
| 8    | A2 B1 C0  | 2.8884 2.8476 2.8992  | 9.18224 |
| Sum  |           | 83.6525  | T  9.29811 |

The results on the S/N ratio values on brown part density then was plotted to obtain optimum parameter of thermal pyrolysis as shown in figure 8. Without taking consideration of any interaction between the parameters, the optimum parameters to produce the highest density can be articulated by choosing the highest mean of S/N value of each parameter based on the plot of figure 6. The result was found that A1, B1 and C0 which means the heating rate of 5 °C/min at temperature 510 °C in 90 minutes period of time during the thermal pyrolysis were the best set of factors.

3.3. Analysis of variant (ANOVA)

Table 5 is the ANOVA for optimization of thermal pyrolysis for density of brown part sample. Heating rate factor (A) gives the highest percentage toward the thermal pyrolysis process which was 54.63 % followed by time factor (C) and temperature of thermal pyrolysis factor (B) which were 24.20 % and 19.25% respectively. The ANOVA results were not taking into account since all parameters factor are above 90% confidence interval. Factor B and C were recorded above 90 (α=0.1) and factor A was noted above 95% confidence interval interval (α=0.05).

The results of heating rate factor (A) to be the highest percentage contribution for the thermal pyrolysis, indicating that this factor contributes substantial influence to produce the highest quality of brown part sample is similar with previous studies found by many researchers [15-18]. Moderate
heating rate factor (A1) found in optimization process is agreed with previous research by Liu et al. [19] through thermal pyrolysis of brown part using stainless steel 316L powder.

### Table 5. ANOVA of brown density.

| Factor      | Parameter                  | Degree of Freedom, fn | Sum of Squares, Sn | Variance, Vn | F Values, Fn | Contribution (%) |
|-------------|----------------------------|-----------------------|--------------------|--------------|--------------|------------------|
| A           | Heating Rate               | 2                     | 0.08562            | 0.04281      | 31.75**      | 54.63            |
| B           | Pyrolysis Temperature      | 2                     | 0.03017            | 0.01509      | 11.19        | 19.25            |
| C           | Time                       | 2                     | 0.03823            | 0.01912      | 13.18        | 24.4             |
| Error, e    |                            | 2                     | 0.0027             | 0.00135      | 1.72         |                  |
| Total       |                            | 8                     | 0.15672            |              |              | 100              |

Significant level a: 0.01, *:0.025, **:0.05 and +/-:0.1

#### 3.4. Confidence interval and range of optimum performance

The results of confidence interval and range of optimum performance for density of brown part was calculated for another experiment to validate the parameters that has been the highest based the result from figure 8. All factors are significant to determine the optimum performance to produce brown part with highest density as shown as table 6. The optimum performance value was at 9.57 dB and the results of optimum performance which was estimated when replicating the experiment for validation was in range of 9.48 dB and 9.67 dB.

### Table 6. Estimation of performance as the optimum design characteristic: higher the better.

| Significant optimum parameters: A1B1C0 |
|----------------------------------------|
| Optimum performance formula:           |
| $T + (A1 - T) + (B1 - T) + (C0 - T)$ |
| 9.2981 $+$ (9.4072-9.2981) $+$ (9.3780-9.2981) $+$ (9.3867-9.2981) $=$ 9.5376 dB |
| Overall performance:                   |
| 9.9281                                 |
| Confidence interval above 90% level    |
| (a=0.1):                               |
| $\pm 0.0946$                          |
| Range of optimum performance, m:       |
| 9.4790 $<$ m $<$ 9.6682                |

#### 3.5. Confirmation experiment

Table 7 shows replication of experiment for validation of optimized density of brown part on 5 samples through optimum performance of A1, B1 and C0. S/N ratio obtained from this experiment was in the range of optimum performance. To verify the efficiency of thermal pyrolysis optimization, sintering process were performed as shown in figure 9. It shows dimensional difference with 12.5% shrinkage after sintering which is in the expected range for MIM products (up to 15%) [20].

### Table 7. Confirmation experiment.

| Replication | Density | S/N Ratio |
|-------------|---------|-----------|
| 1           | 2.978   | 9.555*    |
| 2           | 2.976   |           |
| 3           | 3.135   |           |
| 4           | 2.967   |           |
| 5           | 2.998   |           |

* S/N ratio above optimum performance range level 90% (a=0.1)
Table 8 displays the density, relative densities, shrinkage, strength and elongation of sintered part. It can be seen all properties are follow the standard of ASTM. The average elongation of sintered bodies obtained in this study was 12.15%. These results are better when compared to the findings obtained by researchers who are using alloy Ti-6Al-4V in the field of PIM as Ibrahim et al. [21] and Shibo et al. [22]. However, there are researchers such as Ferri et al. [23] which gained a better elongation from this study so that it can reach 13.7% while reached up to 14.9% but the density and tensile strength recorded by them were lower than the value obtained in this study.

Table 8. Mechanical properties of sintered part.

| Sample | Density (g/cm³) | Relative Density (%) | Shrinkage (%) | Strength (MPa) | Elongation (%) |
|--------|----------------|----------------------|---------------|----------------|----------------|
| 1      | 4.3732         | 98.05                | 12.3841       | 944.2158       | 8.7406         |
| 2      | 4.3741         | 98.07                | 12.2189       | 924.8317       | 17.6221        |
| 3      | 4.3366         | 97.23                | 12.2210       | 920.6800       | 10.0784        |
| Average| 4.3613         | 97.77                | 12.2747       | 929.9094       | 12.1470        |
| ASTM   | -              | >96                  | 12-15         | >895           | >10%           |

4. Conclusion
The goal of thermal pyrolysis is to eliminate PE binder from the sample through Taguchi method in order to assess the density performance of brown part. Optimum parameters for thermal pyrolysis in this research were: 5 °C/min of heating rate at temperature of 510 °C for 90 minutes period of thermal pyrolysis. ANOVA shows that heating rate has contributed the greatest which is 54.63% at $\alpha=0.05$ confidence level followed by time and temperature which were 24.405 and 19.25% respectively at $\alpha=0.1$ confidence level. Optimum parameters obtained were then validated through replication of thermal pyrolysis process and the morphology SEM to see the effect of pore formation. In addition, the result of sintered properties from thermal pyrolysis optimization revealed a reasonable agreement.

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