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Research paper

Rheological Behaviour of Nickel -Titanium Powder Mixture Feedstock Prepared by Dual Assymetric Centrifuge (DAC) Speed Mixer

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Abstract

Preparation of porous NiTi alloy by Metal Injection Moulding (MIM) requires several important steps, starting from mixing of elemental powders with polymeric binder until the final process of sintering. In this present work, some initial findings on the powder-binder mixture, so called feedstock were investigated. Theoretical density of Nickel, Titanium and NiTi powders which were determined using pycnometer are 8.97 g/cm^3, 4.58 g/cm^3 and 6.36 g/cm^3 respectively. The composition for Nickel and Titanium powders mixture studied was 56wt% Ni - 44wt% Ti or nearly around 50.9at% Ni – 49.1at% Ti and mixing torque analysis performed using a Brabender Mixer suggested two powder-binder volume fractions of 61%vol and 64%vol. The elemental powders of Nickel and Titanium with particle size of 20 µm and 22 µm were mixed along with water soluble binder system comprised of Polyethelene Glycol/Polymethylmetacrylate/Stearic Acid (PEG/PMMA/SA) by a Dual-Asymmetric Centrifuge (DAC) speed mixer. The feedstock prepared was evaluated by flow analysis using Capillary Rheometer at four different temperatures; 120ºC, 130ºC, 140ºC and 150ºC and morphological analysis by scanning electron microscopy (SEM). Results showed that DAC technique used in the present work promoted significantly fast processing of MIM feedstock in comparison with conventional method. Besides, the feedstock prepared exhibited good flow behavior, particularly at the temperature of 140ºC, which is supported by SEM morphology that showed uniform powder-binder bonding.

Keywords: *Nickel Titanium; Rheology; MIM*

1. Introduction

NiTi wires was the first NiTi alloy introduced in biomedical application as an orthodontic treatment, fixing malposition teeth or jaw by utilizing the pseudoelasticity and shape memory affect behaviours[1]. Since then, the development of NiTi alloy has booming rapidly and diversified into different field of applications especially in biomedical applications [1],[2]. The ongoing research of NiTi alloy in biomedical is driven by its mechanical properties, good biocompatibility, pseudoelasticity behavior as well as the shape memory effect [3].
Nowadays, the main attraction of NiTi alloy as biomedical devices is focusing on employing the discovery of porous structure that is similar to human bone structure such as bones and tendons which can minimizes stiffness issue between implant and bone [4],[5]. The idea of creating pore structure that could be altered in terms of percentage, shape and size leads to enhancement in the mechanical properties of porous implant accordingly [6]. A study conducted by Ismail et al. (2012) revealed that the porosities content in the range of 30-80% and size ranged from 100-600 µm are the general biomedical practice for implant approach [7].
The MIM process comprise of four sequential stages; mixing of powder-binder mixture, injection moulding, debinding and sintering to consolidate the metal particles[8]. As MIM enables production of small, complex geometry, precision metallic components in high volume, it has emerged as a cost-effective technique in producing medical implant compared to those conventional methods such as casting and machining[8]. Furthermore, MIM also is capable to produce metallic components having better surface finish and shape along with superior mechanical properties[9].
There are several approaches of mixing metal powder with a binder system to produce a homogenous feedstock. German et al (2005) mentioned that there are two types of mixer; batch and continuous. Double planetary and sigma blade are the examples of batch mixer as heat is applied to melt the powder-binder composition accompanying by high shear movement. For continuous mixer like twin screw extruder, the barrel is heated at melting temperature of polymer as the mixture of metal powder-polymer binder is added into the barrel and simultaneously extruded [10]. Although batch mixer is rather economical, however, it delivers feedstock with highest contamination and least homogeneity than continuous mixer [11]. Compared to both type of mixer, Dual Assymetric Centrifuge (DAC) speed mixer is an ideal option of mixing since it requires little handling job, capable to produce homogenous mixture with minimum contamination in a shorter mixing time [12].
It is crucial to perform a rheological analysis which aids to evalu-

ate the flow behaviours of a feedstock prior to injection moulding stage [13]. One of the crucial factor that helps in producing a homogenous feedstock is the choice of the binder system [14]. In this research, water soluble binder system used consists of PEG/PMMA and SA as the additive, as similar composition used by Ismail et al (2012). This binder system is favourable by many researchers due to its environmentally friendly handling besides it can be removed at low temperature during debinding stage [15]. This paper aims to highlight the feedstock preparation process using Brabender Mixer and DAC, followed by evaluation of the NiTi feedstock at different temperatures using Capillary Rheometer and SEM analysis.

2. Methodology

In this study, elemental powders of Nickel and Titanium with particle size of 20µm and 22µm were used. The powders were manually mixed in a glovebox at composition of 50.9 at% Ni-49.1 at% Ti as referred to work by Ismail et al., followed by mixing using Flack Teck, Inc SpeedMixer™ for ten minutes at 800 rpm with the goal to achieve homogeneity. Prior to compounding of the powder-binder mixture, the Critical Powder Volume Percentage (CPVP) for this composition was determined using a brabender mixer. The oleic acid was added along with mixed NiTi powder until maximum torque analysis was achieved. Water soluble binder system consist of polyethylene glycol (PEG), polymethyl-metacrylate (PMMA) and stearic acid (SA) was used in this study.
The mixture of powder-binder was laid in a plastic container and placed in the speed mixer. Four different speeds; 800, 1000, 1200 and 1400 rpm with a mixing time of 4 minutes at each speed were used. At each interval, the feedstock was stirred approximately for 2 minutes to allow homogeneity and smooth combination of powder-binder mixture. Figure 1 depicts the condition of the mixture before and after the mixing process. The flow behaviour of the feedstocks was analysed using RH2000 Capillary Rheometer of Bohlin Instrument at four different temperatures; 120ºC, 130ºC, 140ºC and 150ºC.

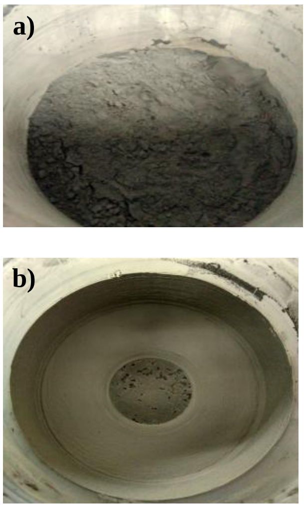

Fig. 1: a) As-mixed NiTi powders before mixing and b) Homogenous NiTi feedstock after mixing by DAC speed mixer

3. Results and Discussion

3.1. Particle Sizes and Density of Powders

The morphology of titanium and nickel powders is displayed in Figure 2 (a) and (b). It is observed that both powders have a spherical shape and consist of a combination of fine and coarse particles. Nevertheless, titanium powder possessed a better spherical configuration compared to nickel powder. Manshadi et al (2017) stated that average of 30 µm and smaller size with fine spherical shape of powder resulted in better performance in terms of flowability, shrinkage rate during sintering as well as the final finishing of the sintered output for MIM process [16].

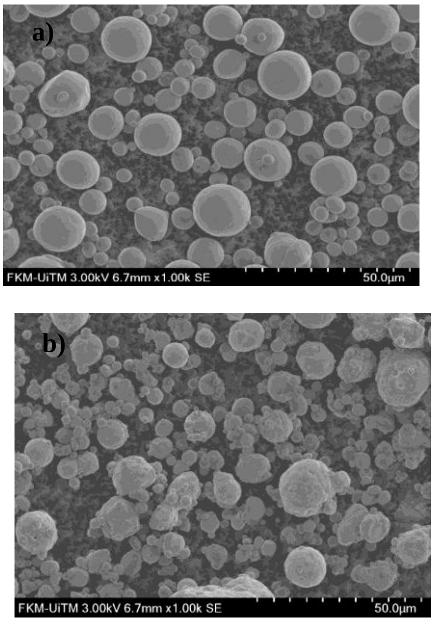

Fig. 2 : SEM images of a) Titanium powder and b) Nickel powder

The particle size distribution and packing density of elemental and as-mixed powders are tabulated in Table 1. The particle size distribution consists of three values which were expressed as D_{10}, D_{50} and D_{90}. Meanwhile, particle width distribution (S_w) is derived from D_{10} and D_{90} where Sw is the slope of log-normal cumulative distribution as in Equation 1 [10], [14]. In this study, the S_w value range from 3.734 to 5.105, indicating narrow particle size distribution despite the range of 4 to 5 (D_{90}/D_{10} = 3.2 to 4.4) which is commonly used in the industry [10].

$$Sw = \frac{2.56}{log10\left(\frac{D_{90}}{D_{10}}\right)} \quad (1)$$

The density of nickel, titanium and as-mixed NiTi powder was determined by apparent, tap and pycnometer techniques. Apparent density represents density at loose condition unaccompanied by agitation while tap density is obtained by vibration of powder at its highest density [11]. Pycnometer or theoretical density is determined using Accupyc under the flow of Helium gas.
Based on Table 1, tap density of nickel powder is 4.76 g/cm^3, which is 53.07% from the theoretical value. Titanium powder indicates higher tap density with value of 57.21% of theoretical density. This could be due to smoother spherical particle surface compared to nickel powder, thus create less particle friction as shown in Figure 2. Meanwhile, as-mixed NiTi represent highest tap density of 4.36 g/cm^3 which is equivalent to 68.55% from theoretical value. Higher packing density is preferable in MIM as it demonstrate higher powder loading during moulding where the shrinkage issue associated with debinding and sintering stage can be minimized [12].

Table 1: Particle Size and Density of Powders

Powder	Particle Diameter (µm)			Packing Density (g/cm^3)			Particle Width Distribution (S_w)
	D_{10}	D_{50}	D_{90}	App	Tap	Pycno	
Ni	5.82	12.67	28.21	3.52	4.76	8.97	3.73
Ti	6.98	12.75	22.14	2.15	2.62	4.58	5.11
Mixed NiTi	6.97	14.53	29.97	2.51	4.36	6.36	4.04

3.2. Critical Powder Volume Percentage (CPVP)

In this research, the powder loading was determined using CPVP by analyzing the mixing torque of the powder-binder mixture. Fig. 3 shows the mixing torque analysis for as-mixed NiTi powder as oleic acid acted as binder. The oleic acid was added every 3 minutes and the mixing torque achieved a maximum torque value or critical solids loading at 14 ml of oleic acid content. Based on Equation 2 which derived the relationship between volume of oleic acid (V_f) and volume of powder (V_o), the CPVP obtained is 66.15vol%, Ideally, the optimum powder loading required for MIM is in the range between 2% to 5% lower than the critical powder volume [17] & [13]. Hence, powder loading for feedstock preparation used in this research were composed of 61vol% and 64vol%, respectively

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$$\text{CPVP} = 100\ x\ \frac{Vf}{(Vf+Vo)} \tag{2}$$

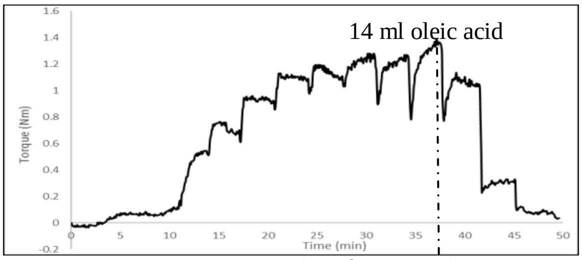


Fig. 3: Mixing torque analysis for as-mixed NiTi

3.3. Rheological performance of NiTi Feedstock

The feedstock preparation which was based on the powder loading acquired by mixing torque analysis was performed using a speed mixer. The rheological analysis was performed on both feedstock; 61vol% and 64 vol% at four different temperatures; 120ºC, 130ºC, 140ºC and 150ºC based on research work by previous researcher [18]. Fig. 4 shows the relationship between shear viscosity and shear rate where viscosity decreases as shear rate increases. Generally, this pattern indicates pseudoplastic behavior or shear thinning effect of the feedstock.

Overall, the viscosity values at different temperatures are below 1000 Pa.s. However, the values obtained at 150ºC for 61vol% powder loading and 120ºC for 64vol% powder loading are slightly higher than the maximum range. Rheological analysis performed by Ismail et al. (2012) at temperature range from 100-140ºC, acquired viscosity values which were lower than 1000 Pa.s [19]. At most temperatures, higher powder loading resulted in greater shear viscosity compared to lower powder loading.

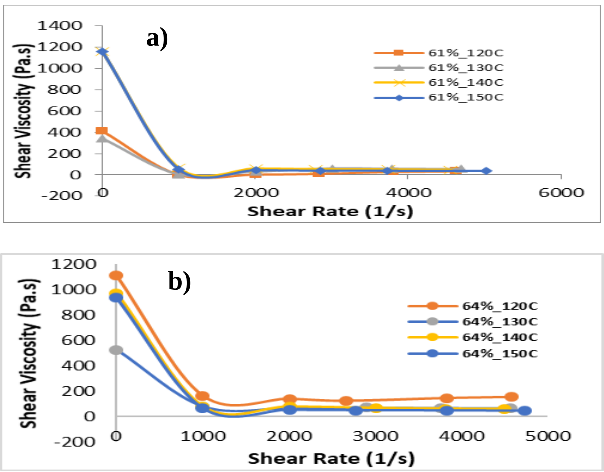


Fig. 4: Relationship between viscosity and shear rate a) Feedstock 61vol% and b) Feedstock 64vol%

Fig. 5 displays the relationship of log shear viscosity and log shear rate. At this point, the shear sensitivity index (n) can be calculated based on Eq. 3 where it shows the correlation between viscosity η and shear rate $\dot{\gamma}$ for the MIM feedstock while K is a coefficient and n is a shear sensitivity index (<1).

$$\eta = K\gamma^{n-1} \tag{3}$$

The shear sensitivity index (n) desirable for pseudoelastic flow behavior and good mouldability is ranged between 0.5 to 0.7. The summary of n values for both feedstocks is shown in Fig. 6. The 64vol% feedstock shows good flow behavior at all temperatures, which are 130ºC, 140ºC and 150ºC. At the highest temperature, the shear sensitivity index indicates the lowest value due to swelling of the extruded sample as mentioned by Ismail et. al [5]. On the other hand, the 61vol% feedstock shows good flow behavior at temperatures of 140ºC and 150ºC while at 130ºC, the n value is slightly higher than the acceptable range. The findings suggest that feedstock with powder loadings 64vol% exhibited excellent flow condition at all temperatures. Meanwhile, feedstock with powder loading 61vol%, possessed a slight viscous behavior at 130ºC and slight swelling at 150ºC. By taking into consideration the flowability of feedstock for both powder loadings, a temperature of 140℃ has been found as the most ideal temperature for injection moulding of the feedstocks. Generally, it can be concluded that the shear sensitivity index (n) decreases as temperature increases.

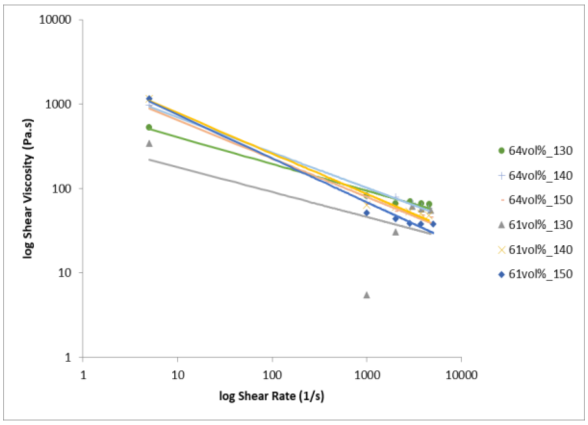


Fig. 5: Log shear viscosity versus log shear rate

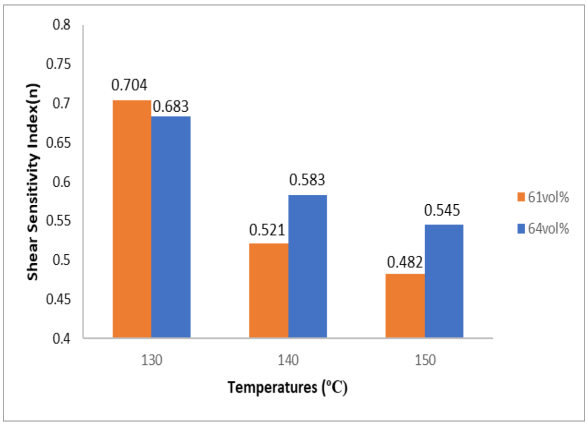
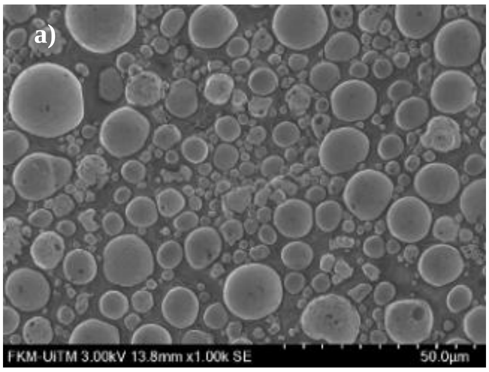


Fig. 6: Shear sensitivity index (n) for feedstock 61vol% and 64vol%

Following the rheological analysis, morphological analysis of the extruded feedstock was analyzed using SEM. As shown in Fig. 7, the feedstock with higher powder loading, 64vol%, showed greater packing as the metal powder particles were less occupied by binder constituent compared to the one with 61vol% powder loading. A greater ratio of powder to binder in turns increased the shear viscosity of the feedstock[16]



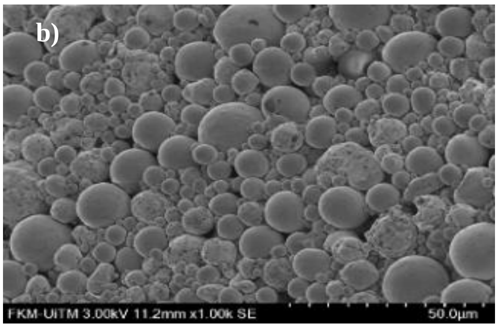


Fig. 7 : SEM images of a) feedstock 61vol% and b) feedstock 64vol%

4. Conclusion

In conclusion, the critical powder volume percentage (CPVP) method performed using Brabender Mixer resulted in two powder loadings, 61vol% and 64vol%. Homogenous feedstocks with composition of 50.9 at% Ni-49.1 at% Ti had been successfully produced using Dual Assymetric Centrifuge (DAC) or Speed Mixer by employing water soluble binder system PEG/PMMA/SA. Rheological analysis of the NiTi feedstocks exhibited reduction of viscosity with increasing shear rate at all temperatures, suggesting shear thinning effect or pseudoplastic behavior. The shear sensitivity index values for 64vol% powder loading are in the range of 0.5 to 0.7 for all temperatures, indicating suitability for injection moulding process. Meanwhile, for 61vol% powder loading, the n value of 0.521 which is suitable for injection moulding is observed at 140ºC. The findings suggested that a temperature of 140ºC is the most optimum heat input for injection moulding of both composition of powder loadings. In term of morphologies, 64vol% powder loading shows higher packing particles than 61vol% powder loading, implying higher viscosity.

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Project Title: Fabrication of Porous NiTi Dental Implant by MIM
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Project Title: Porous Pseudo-Elastic NiTi Dental Implant by Advanced MIM Process

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