International Journal of Emerging Technology and Innovative Engineering
Volume 1, Issue 7, July 2015 (ISSN: 2394 – 6598)

DEBINDING AND SINTERING CHARACTERISTIC OF INJECTION MOULDING CoCrMo ALLOY POWDER FOR BIOMEDICAL APPLICATIONS

M.A.OMAR
AMREC, SIRIM Bhd
Lot 34, Jln Hi Tech 2/3
Kulim Hi Tech Park, Kulim,
Malaysia
afian@sirim.my

R.SAUTI
AMREC, SIRIM Bhd
Lot 34, Jln Hi Tech 2/3
Kulim Hi Tech Park, Kulim,
Malaysia
pink_minwat@yahoo.com

N.ABDULLAH
AMREC, SIRIM Bhd
Lot 34, Jln Hi Tech 2/3
Kulim Hi Tech Park, Kulim,
Malaysia
syakira@sirim.my

ABSTRACT
The present study investigates the processing characteristics of injection moulded gas atomised CoCrMo alloy powder powder using new developed binder system based on palm stearin. Model experiments were conducted with new palm-based biopolymer binder system consists of palm stearin and polypropylene. The feedstocks having 65 vol. % of metal powder were injection moulded into a test bar. A rapid two stage debinding process involving solvent extraction and thermal pyrolysis was successful in removing the palm stearin binder in short time. The specimens were then sintered under vacuum atmosphere at the temperature range of 1360°C to 1400°C. The sintering studies were conducted to determine the extent of densification and the corresponding microstructural changes. In addition, the properties of the sintered specimens such as physical appearance, microstructure evolution and mechanical properties were presented and discussed.

General Terms
Sintering.

Keywords
Metal injection moulding, debinding, sintering, CoCrMo powder.

1. INTRODUCTION
Metal injection moulding (MIM) has been widely recognised as an advanced technology for the fabrication of complex-shaped, low cost and high performance components. Fine powders, less than 20 micron in diameter, are mixed with suitable thermoplastic binder and formed into the desired shapes. The binder aids the flowability and formability of fine metal powders during moulding, and they have to be removed in the next stage to enable high density components to be produced. The removal of the binder is done either thermally in the furnace or by solvent extraction. Ideally, the removal of the binder would open up pore channels which allow accelerated removal of the higher boiling point components. The components are sintered following the debinding stage. This stage is crucial to the MIM process as appropriate sintering conditions would ensure pore-free structures that have good mechanical properties. [1,2,3,4]

Theoretical studies of sintering treat the powder as a spherical particle and divide sintering into three stages. The early stage of sintering occurs at low temperatures and is characterised by neck growth at the contact points between the particles. The intermediate stage of sintering is characterised by an interconnected pore system having complex geometry. The final stage begins when the pore phase becomes closed and the shrinkage rate of the components slow down. This final stage characterised by pores on four-grain corners that shrink rapidly, and sphereodised powders that separate from grain boundaries and shrink slowly. When all pores on four-grain corners have been eliminated, sintering densification essentially ceases. [5,6,7]

In previous work, a binder system comprised of paraffin wax and thermoplastic binder (polyethylene and polypropylene) as a backbone polymer was successfully mixed and injection molded and has been study by many researchers in the world [3,4,5,6,7] The present study examines the densification process development of MIM gas atomized CoCrMo alloy powder using novel palm based biopolymer binder for medical applications. Palm oil derivative, commonly known as palm stearin, has a major potential application as a component in a binder system in powder injection molding (PIM) process, since it consists of a fatty acid which is commonly used as a surface active agent for many binder systems. Its potential attributes such as low cost, low viscosity and locally availability, have stimulated exploration of its feasibility in the MIM process.

2. EXPERIMENTAL PROCEDURE

2.1 Powder Characterization and Binder Formulations

The CoCrMo alloy powder used in the present study was obtained from Sandvik. The mean particle size distribution was determined using HELOS Particle Size Analysis WINDOX 5 and around 9 micron A scanning electron micrograph showing the powder morphology is indicated as spherical. The powder was mixed with a natural polymer based binder (palm stearin) at a solid loading of 63volume % for injection molding. The binder system consists of 70-weight % of palm stearin and remaining 30-weight % of polyethylene, which represent the remaining 35-volume %. Mixture of powder and binder were dry mix followed by the entry into the Z-Blade mixer heated to 160^{o}C. The mixing was left for 1 ½ hour. After mixing has completed, the heater was shut off and the feedstock was allowed to cool with the mixing blade still in motion. This procedure gives a granulated feedstock.

2.2 Injection Moulding of the Feedstock

The granulated feedstock then injected into tensile bars using a simple, vertically aligned and pneumatically operated plunger machine, MCP HEK-GMBH. Feedstock was fed into the barrel and then injected through the nozzle in the mold cavity. Test bars were successfully molded at temperature of 200^{o}C at pressure 300 bar. The dimensions and weight including density were measured in order to determine the solvent removal and shrinkage after sintering. The densities of the specimens were measured using water immersion method.

2.3 Debinding and Sintering Process

The test bars were debound by a two-step process where at the first stage the samples were solvent debound in order to remove all the wax portion of the binder, in this case palm stearin which is consist the major fraction of the binder. Molded samples termed the green body were arranged in a glass container, which then immersed in heptane and held at temperature 60^{o}C for 5 hours. The glass container was covered to prevent evaporation of the heptane during extraction. Subsequent thermal pyrolysis was performed in Lynn Furnace. The thermal debinding cycle consisted of 1^{o}C/min to 450^{o}C and soaking for 1 hour before furnace cool. Sample that completely undergoes thermal debinding termed the brown body. The components were sintered in vacuum furnace with the heating rate at 10^{o}C/min to the sintering temperature 1400^{o}C, and held for 1 hour at this temperature before cooled down by furnace cool.

The dimensions, density and weight of the sintered specimens were measured to calculate sintered shrinkage and final density. Tensile properties of the sintered samples were determined using an Instron Series IX Automated Materials Testing System. The yield strength, ultimate strength and elongation were measured at strain rate of 0.1/s [7]. Finally, the microstructure analysis carried out using optical microscopy and scanning electron microscopy.

3. RESULTS AND DISCUSSION

3.1 Rheological Properties of the Feedstock

In MIM, the rheological properties are important for the injection molding step as it concerns the flow of the feedstock during injection moulding. Rheological analysis can be used to quantify the stability of the feedstock during the moulding process [1].

The viscosity of the powder-binder mixture is very sensitive to temperature and powder loading (amount of powder). At low temperatures, the mixture viscosity may be too high for moulding. At high temperature, the binder may be too thin, resulting in powder-binder separation during moulding. Besides, the binder may undergo degradation with substantial thermal stress in the moulded parts resulting in cracking. Hence, there is a range of conditions over which the MIM processing is most viable. In this range, the mixture exhibits pseudo plastic flow where the viscosity decrease with increasing shear rate and this can help to reduce the required temperature and pressure for successful moulding [2,3]. Pseudo plastic flow behaviour eases mold filling, minimize jetting and help to retain the shape of the molded part. Generally, high packing density is desired. It is well established that viscosity varies with the relative powder loading.

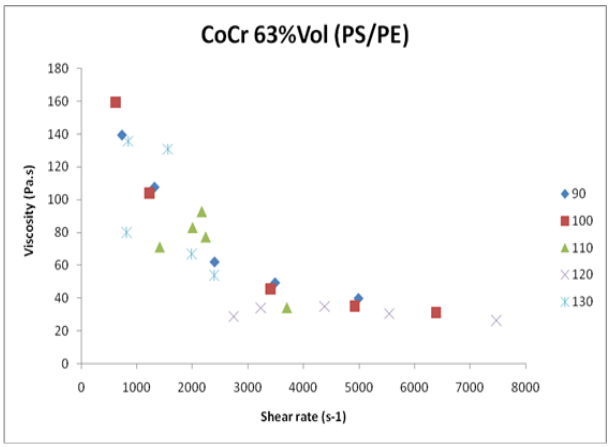


Fig. 1: The graph of viscosity versus shear rate for 63vol.% of powder loading formulations of PS and PE at different temperatures

The graph of viscosity versus shear rate for 63vol.% of powder loading formulations of PS and PE at different

temperatures are shown in Figure 1. It shows that increasing the shear rate results in decreasing the viscosity which is favourable with pseudo plastic flow. Almost all data exhibited good viscosity even at a high temperature tested of 130 ^{o}C. The range of viscosity is between 1200 and 200 Pa.s. The feedstock containing PS/PE binder system has a good fluidity at high temperature. This can be observed during the experimental work at 110 ^{o}C to 130 ^{o}C.

3.2 Injection Moulding of Feedstock

After several trials and error, the feedstock was successfully injection moulded at the nozzle temperature of 200^{o}C and injection pressure of 300 bar. Total cycle time for each injection was 6 seconds. Figure 2 shows the tensile shape of the injection moulded parts with a single gate, located at one end of the part. The moulding temperature used during the study can be considered as much higher as compared to other reports, which commonly used at the range of 100^{o}C to 200^{o}C [4-10]. Nevertheless, during the injection, all injection parts were fairly good and free from normal defects such as short shot, flashes at the parting surface and binder separation. The higher temperature applied was believed to the high viscosity of the feedstock. In order to make sure the feedstock can be easily flow and moulded, higher temperature was needed to compensate the high viscosity of the feedstock.

Fig. 2: The tensile shape of the injection moulded parts with a single gate, located at one end of the part

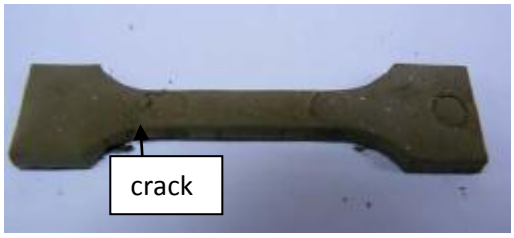
The average green density of green parts is 5.01 g/cm^{3}. This result is 63 % of theoretical density. The lower green density of the moulded parts associated with poor packing property of the powder. However the parts are free from normal defects.

3.3 Debinding Process

To minimize the possibility of defects with safe and fast binder removal, solvent debinding followed by thermal debinding was used. The multi-component binder chosen includes the lower stability components of palm stearin wax which is removed in early stage of debinding and generate pore channels inside of the part that allow gaseous products of degradation of remaining binder harmlessly diffuse out of the structure while PE has a function of holding particles together during and after extracting lower stability components to maintain the part shape. Solvent debinding was carried out by means of heptane as a solvent at 60 °C only for 5 hours. It is considered that after removing 40% of binder, there exists some interconnected capillary porosity inside of samples which makes leaving of gaseous products in subsequent thermal debinding easy in short time. Since nearly 70% of palm stearin was removed in solvent debinding step, subsequent thermal debinding can be performed with higher speed in comparison with usual thermal debinding process.

Different heating rates and sintering environment were performed to optimize the suitable heating rate can used later. Four different heating rates were used from 0.1ºC/min to 5ºC/min to select for debinding process. It was observed that at heating rates 0.1°C/min, 0.5°C/min, 1°C/min and 3°C/min were study to optimise the thermal pyrolysis stage up to 450°C. It was shown that only 0.1°C/min gave the best appearance without any blistering on the surface, as shown in Fig. 3a. However, when the heating rate was increased to 0.1 to 1°C/min the swelling and cracks appeared on the surface of the test samples as shown in Figure 3b. A slow debinding was necessary to allow gaseous products of the decomposition reactions to diffuse out of the specimens. This will avoid excessive pressure build-up, which can cause cracking and introduces other defects

a



b

Fig. 3: Brown specimens after thermal debinding with different heating rate at a) 0.1 °C/min and b) 1°C/min

3.4 Sintering Process

No defects such as cracks, distortion which might affect the properties were observed in the sintered samples. Figure 4 shows the relationship between sintering

temperature and the density. As the sintering temperature increased, the sintered density, as expected, increased. The pores become more rounded. Consistent with increasing density, the measured ultimate tensile strength increased with increasing sintering temperatures

This powder is usually sintered slightly above its solidus temperature; however, the solidus temperature varies depending on composition, especially carbon content [1]. The high packing density of the powder resulted in high final density that is 8.30 g/cm^3. As can be seen, the samples average density is almost the same as ASTM F75 density, which is more than 8.20 g/cm^3. As expected with the decreasing in porosity, increased the sintering temperature improved the sintered density and ultimate tensile strength. The optimal sintering temperature was 1390^{o}C.

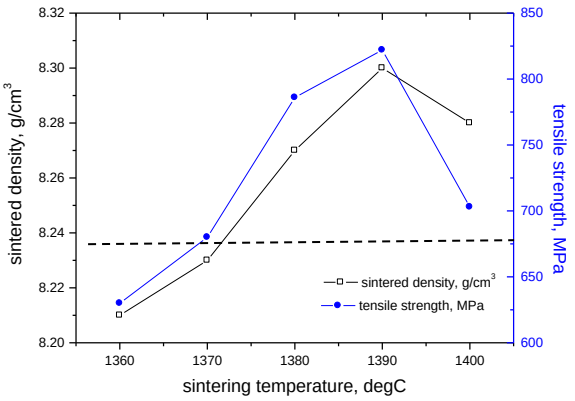
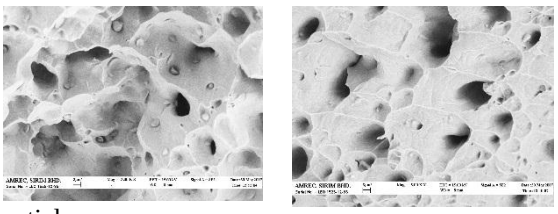


Fig. 4: The effect of sintering temperature on sintered densities and ultimate tensile strength

The drastic increment in strength value was obtained when specimens were sintered at 1360^{o}C to 1380 ^{c}o. These might be due to the changes occurring, from early stage to intermediate stage of sintering that undergoes a transformation to become dense and pore channel closure, with attendant changes in the pore size and shape. Meanwhile, sintering at 1380^{o}C inherently involves substantial shrinkage with elimination of pores that lead to a dramatic increase in strength of all specimens. The optimal sintering temperature was 1390^{o}C. After this, the properties of the sintered sample decreased due to the samples distorted and slumping.

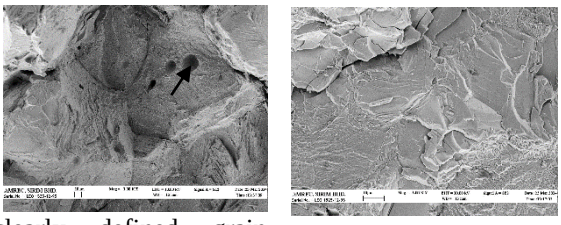
The fracture surface of specimens sintered in different temperature were observed by SEM. Figure 5 depicts the SEM micrographs of vacuum sintered SS 316L specimens. Figure 5 (a) shows the powder boundaries were replaced by grained boundaries. As the temperature increase, the microstructure began to coarsen and the grains began to grow, the fracture morphology shows obvious inter-grain-boundary fracture characteristics. In the intermediate stage as in Figure 5 (b), both close pores and open pores connected together can be observed. These open pores connected together are attributed to lower elongation of specimens sintered at the temperature corresponding to the intermediate stage than that of the specimen corresponding to the final stage. The typical ductile fracture mechanisms evidenced by dimples is noted in the final stage of sintering as in Figure 5 (c) and (d). A few isolated pore (closed pores) can be observed as indicated by arrow in the Figure, suggesting that closed pores play little part in the fracture. The included



particles appear undeformed

Fig. 5: SEM micrograph of fracture surface, sintered at 1390 ^{o}C showed a dimple morphology.

Microstructure of the etched samples sintered at 1390 ^{o}C in vacuum is shown in figure 6. Etching results in



clearly defined grain boundaries, indicating that they are chemically different from the grains.

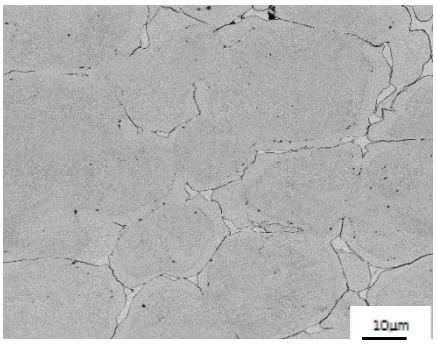


Fig. 6: The microstructure of CoCrMo alloy after etching.

4. CONCLUSIONS

The experimental results found in this study indicate that CocrMo alloy powder could be injection moulded using multi-component binder system comprising of palm stearin (PS) and polyethelene (PE). The results obtained from solvent extraction process by means of n-heptane at 60°C, suggests that PS is a very effective ingredient for effectively reducing the overall debinding time of CoCrMo injection molded parts. Optimized sintering was observed to take place at a temperature of 1390°C, resulted in 99.7 % of the theoretical value due to sufficient amount of liquid phase generated. The microstructure was dense and shows typical ductile fracture mechanism. This observation corresponds to its tensile strength of more than 700 MPa which is comply with the standard of ASTM F75

5. ACKNOWLEDGMENTS

The authors wish to thank MOSTI for financial support under Science Fund grant no. 03-03-02-SF0247 and SIRIM Bhd

6. REFERENCES

[1] German. R.M. and Bose, A 1997. Injection Molding Of Metals and Ceramic, Metal Powder Industries Federation, Princeton, New Jersey.

[2] German, R.M. 1990. Powder Injection Molding, Metal Powder Industries Federation, Princeton, New York.

[3] Mohd Afian Omar, 2013. Metal Injection Moulding Process: An Advanced Processing Technology , *Metal Injection Moulding of Implants Materials* , Chapter 1, ISBN 978-967-11588-1-4.1-16

[4] John L. Johnson and Lye King Tan. 2000. Processing of MIM CO-28Cr-6Mo, Advances in Powder Metallurgy. 13-19.

[5] Marti, A. 2000. Cobalt Based Alloys Used in Bone Surgery, Injury, Int. J. Care Injured 31, S-D18-S-D21

[6] Omar, M.A. Abdullah, N., Roslani, N., Zainon, M.N., and Meh,B. 2011. Development of injection moulded Co-Cr-Mo alloy powder using palm based binder. *Solid State Science and Technology*, Vol. 19, No2. 61-69

[7] Omar, M. A., Ibrahim, R., Sidik, M.I., Mustapha, M., Mohamad, M., 2003. Rapid Debinidng of 316L Stainless Steel Injection Moulded Component, Journal of Materials Processing Technology, 140, 397-400.