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APPLICATIONS OF PALM STEARIN AS A BINDER FOR INJECTION MOULDING OF BIOCOMPATIBLE MATERIALS

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ABSTRACT

A binder system is successfully developed for metal injection moulding of biocompatible materials, CoCrMo alloy powder The binder comprises a major fraction of palm stearin, which can be removed rapidly by solvent extraction and a minor fraction of polyethylene or polypropylene, which retains rigidity of the components. PE or PP can be removed by pyrolysis during ramping up to sintering temperature. Studies have been made to the feedstock compositions and to the process parameters in order to achieve high density components. Feedstock having a powder loading of the CoCrMo powder mixture up to 65 vol. % can be injection moulded successfully. Specimens can retain shape their shape during and after debinding. The final density achieved is higher than 97% of theoretical density and show a good mechanical properties.

INTRODUCTION

Since 1980s when major attention was given to metal injection moulding (MIM) process, it has been widening the application area from small parts with complex shape and tailored properties to structural parts requiring strength and ductility as in automotive, military and medical industries. MIM is composed of four main processes starts with mixing of metal powder with a polymer, then followed by injection moulding the mixed feedstock into desired shape, removal of the polymer binder and sintering. To achieve near full density of sintered components, the binder must be removed completely from the green compacts prior to the sintering process, therefore the compact damage and the binder remaining can be avoided [1,2].

The binder provides the powder with the fluidity necessary for moulding. It also strongly influences the maximum solid fraction of the mixture that can be moulded, the green strength of the moulded part and the properties of the final products after debinding. Successful production of parts by the MIM process is closely related to the formulation of the binder for use with the powders. The role of the binder is to serve as a temporary or transient phase to impart flowability and moldability. This will enable the shaping of the feedstock to the required shape during injection moulding [1,2].

A critical issue for metal injection moulding (MIM) binder at the present is the vapours given off during mixing, moulding and debinding, which can cause irritation to eyes

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and respiratory system and damage the environment. Furthermore, most of the binder is expensive and imported from overseas. Hence, there has been a considerable motivation to design and develop binders that are safe in practice, locally produced, cheap and present fewer health hazards to employees and environment during processing. There is a clear requirement for a binder system that combines good forming and debinding performance with environmental acceptability.

To overcome at least some of the problems associated with the other system, a locally produced composite biopolymer binder system had been investigated. These consist of palm stearin and thermoplastic polymer.It is believed that this new binder system can be developed to replace the conventional binder systems which mainly comprise of three to four components. On top of that, palm stearin has many suitable properties such as low cost, low viscosity, high decomposition temperature, easily dissolve into organic solvent and highly available in Malaysia.

The objective of the present study is to investigates the influence of palm stearin content with the aim of using palm stearin as a based binder system and how this affects the moulding behaviour and the properties of the moulding, debinding process and sintering. A CoCrMo alloys ha sbeen chosen as a model biocompatible materials because commonly used for surgical implants. This is because of their high strength, superior corrosion resistance, non-magnetic behavior and biocompatibility [3,4]. Applications include prosthetic replacements of hips, knees, elbows, shoulders, ankles and fingers, bone plates, screws, staples, and rods; and heart valves . Joint endoprostheses are typical long-term implants, and the applied implant material must therefore meet extremely high requirements with regard to biocompatibility with the surrounding body tissue material and corrosion resistance to body fluids. Various in vitro and in vivo tests have indicated that the alloys are biocompatible and suitable for use as surgical implants [5].

METHODOLOGY

Powder characteristics

The Co-Cr-Mo 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 given in Table 1. A scanning electron micrograph showing the powder morphology is indicated is Figure 1.

Table 1: The cumulative particle size distribution of stainless steel powder.

Fraction (%)	<10	<50	<90
Size (m)	3.47	9.72	20.73

Mixing

The powder was mixed with a natural polymer based binder (palm stearin) at a solid loading of 65-volume % for injection molding. The binder system consists of 70-weight

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% 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.

Rheological Behaviour and Injection Molding
The rheological behavior of the feedstock that completely granulated then studied before injection molding was done. This procedure is important where the flow rate and viscosity of feedstock could be obtained. Rheology behavior was studied and evaluated using Capillary Rheometer.

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 220^{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.

Debinding and Sintering
The test bars were debound by a two-step process where at the first stage the samples were solvent debound in order to removed 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. The same procedure applied for solvent kinetics study for time ranging from 10 minutes to 300 minutes. After completing solvent debound, the extracted bars were left drying in oven temperature at 40^{o}C for 4 hours to removes the remaining heptane. After drying, the weights of the extracted samples were measured to calculate binder removed.

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 1390^{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 [6]. Finally, the microstructure analysis

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carried out using optical microscopy and scanning electron microscopy.

RESULTS AND DISCUSSION

Powder Characteristics

The results of the powder characterization are shown in Table 1. The mean particle size is 9.72 m. while the particle size distribution, S_W value is 3. The ideal metal injection molding (MIM) particle size is between 0.5 and 20 m with D_{50} is between 4 to 8 m. the particle size distribution, SW is represent by the equation (1):

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

Correlation of PIM behavior shows the best powders have narrow size distributions [1]. It is clearly determined that the powder has relatively wide particle size distribution between 3 m and 20 m, which is desirable for effective particle packing. The particle size distribution, S_W value should be smaller which represents very broad particle distribution for better packing and sintering shrinkage. These CoCrMo powder characteristics are somewhat are well aligned with the desired values for MIM powders.

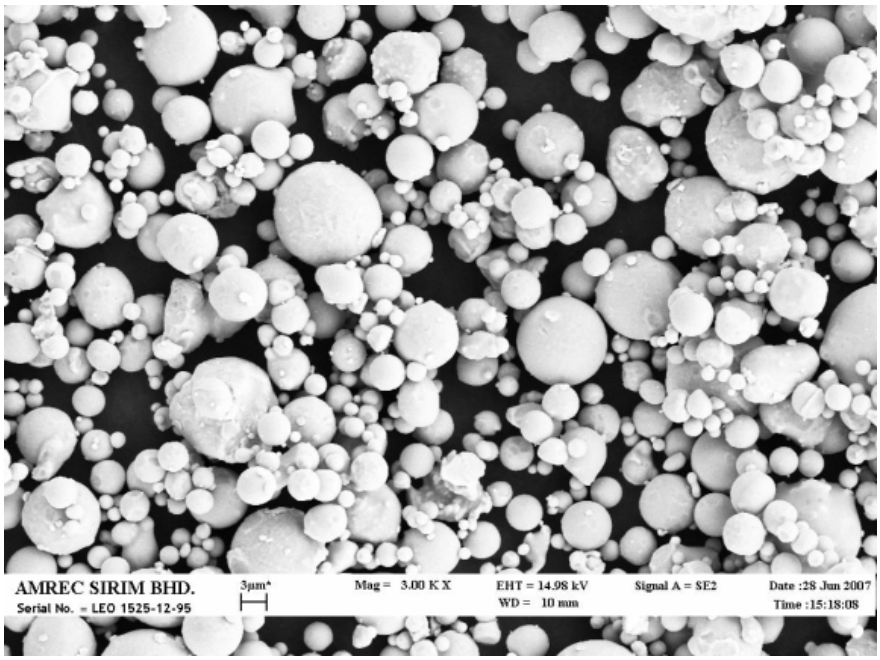

Figure 1: A scanning electron micrograph of 22 µm F75 Co-Cr-Mo powder.

All the particles were approximately spherical, as indicated in Figure 1 Some particles are large spheres and some are very small. Easier molding and a high solids loading are favored by spherical particles [1,2]. The spherical shape of the particles will result in

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higher packing density, easier molding. Small particles agglomeration is a common problem. Nevertheless, with the presence of the larger particles will reduce the agglomeration problem where the smaller particles will fill the voids between the large particles without forcing the large particles apart.

Rheology and Injection Moulding

MIM feedstock should indicate viscoelastic behavior. This characteristic is most important during cooling after molding, since cooling rate will determine final stresses [1,2]. However, most injection molding feedstocks exhibit more complex behavior, producing viscosity that depends on the shear rate as well as pressure and temperature, generally decreasing at higher shear rate. This condition termed as psuedoplastic behavior. The viscosity of a psuedoplastic substance decreases as the shear rate increase (shear tinning) [2].

Table 2: Rheology properties for coarse powder at different load and temperature.

Temperature, ^{o}C	**Load, N**	**Shear Rate (s^{-1})**	**Viscosity (Pa.s)**
100	60	3.333E+02	6.085E+03
	70	2.961E+02	5.859E+03
	80	1.157E+03	4.240E+03
	90	2.261E+03	1.483E+03
110	40	9.898+02	1.845E+03
	50	2.148E+03	6.061E+02
	60	3.917E+03	9.982E+02
	70	6.697E+03	2.738E+02
120	40	1.580E+04	6.284E+01
	50	1.661E+04	7.383E+01
	60	1.738E+04	8.463E+01
	70	1.751E+04	9.806E+01
130	40	1.655E+04	5.941E+01
	50	1.723E+04	7.119E+01
	60	1.739E+04	8.460E+01
	70	1.620E+04	1.064E+02

In capillary Rheometer, the pressure drop associated with a forced flow rate through a small capillary tube is measured. From the results (Table 2) we found that the viscosity data for the powder tested at the above-mentioned temperature were in the region of 10 to 1000 Pa.s and show a psuedoplastic behaviour, which is desirable for MIM application. Empirical studies have shown that the shear rate during molding usually

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ranges between 100 and 10,000 s-1 and maximum viscosity for molding is 1000 Pa.s at the molding temperature [1,2].

The testing at temperature of 130^{o}C giving a slight decreased of viscosity as shear rate increased. Still, the viscosity falls within the range of 10 and 1000 Pa.s although the values absolutely differ from 100^{o}C and 110^{o}C data. Meanwhile for testing with 120^{o}C resulted in dilatant flow which the viscosity increased with shear rate. This is undesirable for MIM because of possible powder-binder separation in molding [6]. This situation will caused the feedstock flow being stuck because of the high shear force.

After several trials, the feedstock made with the PS/PE binder system was easily moulded at optimum injection moulding parameter as shown in Table 1. All the injection parts were quite good and free from normal defects such as short shot, flashes at the parting surface and binder separation.

Table 3: Optimum injection moulding parameters of machines used in this study

MCP HEK-GMBH Injection Moulding (Vertical Injection Moulding)
Temperature: Nozzle : 220^{o}C Mould : room tempearure
Injection pressure : 30 MPa (300 bar)
Cycle time : 10-20 seconds
Part produce : tensile bar

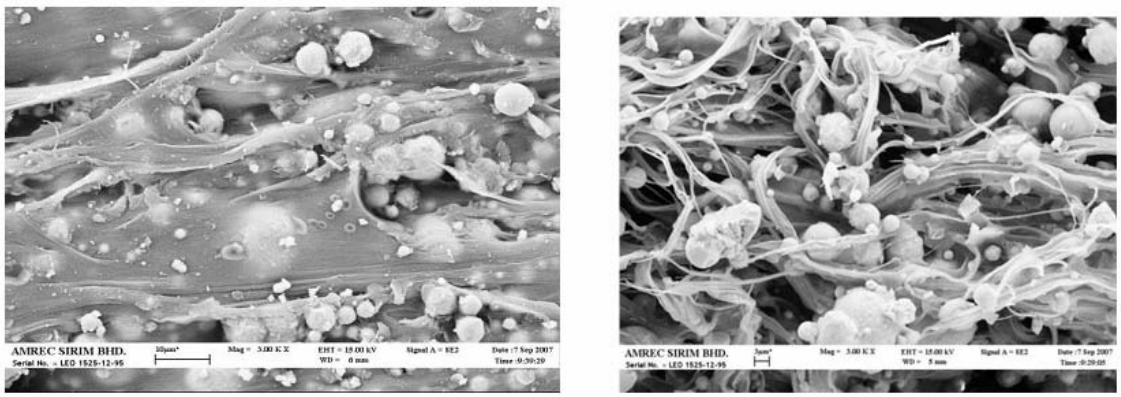

Figure 2: The scanning electron micrograph of the green body after injection molding.

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Figure 2 indicated a scanning electron micrograph of the green body sample. It can be clearly observed that the binder fills practically the interstitial spaces among the powder particles. As can be seen, there are few voids presences between the particles. The presence of the voids was due to air bubbles that entrapped during mixing or molding. Furthermore, the powders particles are linked to each other by a network of binders consist of polyethylene as the backbone binder together with palm stearin. The networks impart sufficient green strength for the handling prior to debinding and sintering.

Debinding and Sintering

The debinding via solvent extraction method followed by a thermal cycle effectively removed almost all of the binders with minimum possibility of cracks and blisters formation. During debinding, no shape distortion observed and so on after sintering. Binder removal rate can be attained resulting from solvent kinetic test showed that after 120 minutes, most of the palm stearin could be removed from the moulded specimen.

It is considered that after removing 70% of binder, there exists some interconnected capillary porosity inside of the specimen which makes leaving gaseous products in subsequent thermal debinding in short time [7]. The pore channels permit the remaining binder (polyethylene) to diffuse harmlessly during burnt out.

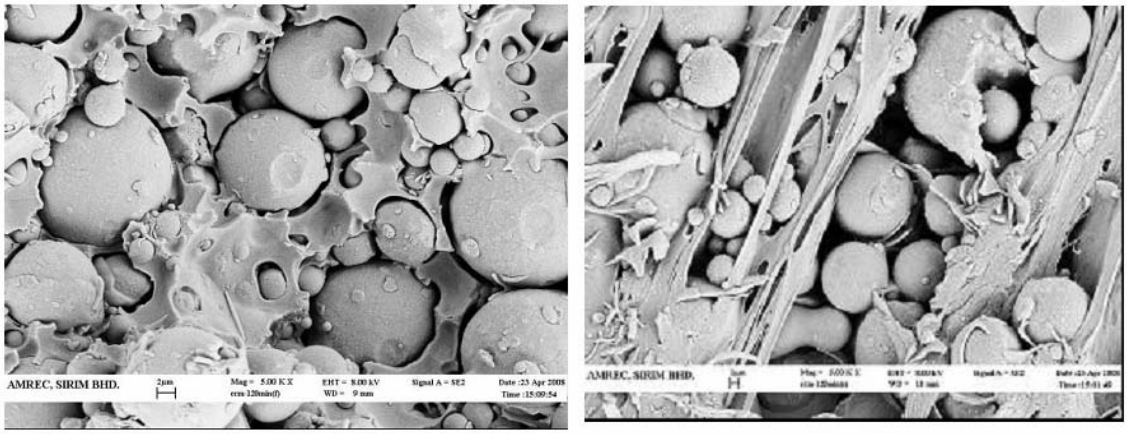

Figure 3: The scanning electron micrograph of solvent debound specimen at 60^{o}C for 120 minutes.

Figure 4 shows scanning electron micrograph of debound specimen after solvent extraction. During solvent debinding, the solvent penetrates the binder phase and dissolves the soluble binder, palm stearin and creates porous surface. The networks of polyethylene remained, binding and holding the powder particles together to provide the molding with sufficient 'brown' strength to be handled. The formation of open-pore channels allows the rapid removal of the remaining binder, i.e. PE without cracking, blistering or swelling during subsequent thermal pyrolysis.

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Figure 4 indicates scanning electron micrograph of sample after thermally debound at 450°C which can be observed that all binders have been removed.

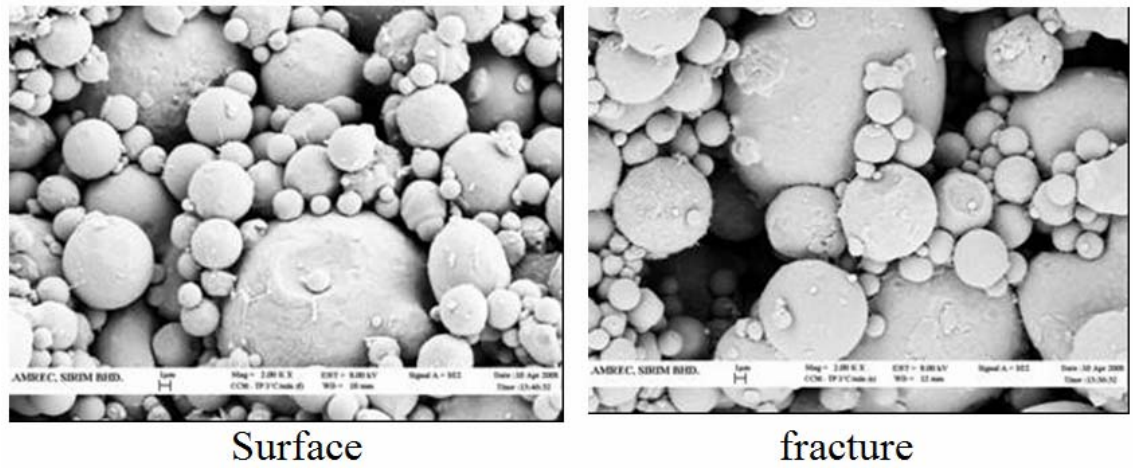

Figure 4: The scanning electron micrograph of thermally debound specimen.

A sintering temperature of 1390^{o}C was chosen for densification of the test bar in vacuum atmosphere. Pores are eliminated as part of particle bonding during high-temperature sintering [1,2]. Sintering densification normally take place close to the me melting temperature of the material, where the bonds of the particles are bonding together by the atomic motion of the individual atoms via either solid state or liquid phase. As the temperature arises, the atomic motion occurs faster. Likewise, sintering temperature differs for each material.
This powder is usually sintered slightly above its solidus temperature; however, the solidus temperature varies depending on composition, especially carbon content [1].

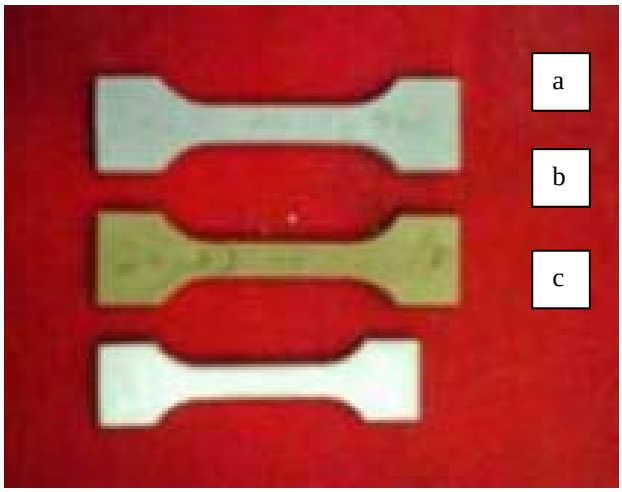

Figure 5: A tensile specimen (a) green body; (b) brown body; (c) sintered sample

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Figure 9 indicated the test bar after molding, which still contains binders, the thermally debound part which consist only powder particles and sintered part having high packing density. Shrinkage of the sintered part clearly observed.

Final Density and Mechanical Properties

Sintered sample properties are shown in Table 4. The high packing density of the F75 powder resulted in high final density that is 8.20 g/cm^3. As can be seen, the samples average density is almost the same as ASTM F75 density, which is 8.28 g/cm^3.

A tensile property of the samples is relatively higher than previous* study by John Johnson and Lye King Tan with tensile value of 822.055 MPa. The sample indicated ductile fracture during tensile test. High rate of densification during sintering resulted in high packing density due to less porosity remain in the sintered body.

Table 4: Sintered properties for F75 Co-Cr-Mo powder.

Samples	F75 CoCrMo	Previous Study*
Density (g/cm^3)	8.20	7.99
% from theoretical	99.03	96.5
Ultimate tensile strength (MPa)	822.005	730
Elongation (%)	10.453	10

CONCLUSIONS

Through some modification on some MIM processes, the MIM process has successfully implemented for the F75 Co-Cr Mo alloy powder. Powder characteristics, mixing and molding is quite a critical stage in MIM. If powder particle has wider range more homogeneous feedstock can be obtained and giving more consistent results during some testing. The physical and mechanical properties achieved comply with the International Standard, ISO 5832-4, implants for surgery.

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