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The Potential Of Starch As An Eco-Friendly Binder In Injection Moulding Of 316L Stainless Steel For Medical Devices Applications

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Abstract. Two starch/wax based binders were formulated for metal injection moulding of 316L stainless steel. The formulations difffer in term of the starch type which substitute the backbone polyethelene. Feedstock having powder loading of the stainless steel powder up to 65 vol.% can be injection moulded successfully. Solvent debinding was performed in water at a temperature of 60^{0}C for 3 hours and followed by immersion n-heptane for duration of 2 hours to remove the residual wax. The remaining binder was thermally extracted at 450^{0} with heating rate of 3^{0}C/min, with no defects. The parts were then sintered in vacuum atmosphere within a temperature range of 1300°C to 1380°C. Approximately, 6.8 g/cm^{3}theoretical density, hardness of 188.8 HV and tensile strength of 229.3 MPawere achieved for cassava starch/wax based binder while rice starch/wax based binder possessed 8.6g/cm^{3}theoretical density, hardness of 385 HV and tensile strength of 462.1 MPa.

Introduction

Biofunctionality and biocompatibility are two sets of characteristics that controlled the performance of any material in the human body. 316L Stainless Steel(SS 316L) is one of the most frequently used alloy in all implants division ranging from cardiovascular to otorhinology owing to their favorable combination of mechanical properties, corrosion resistance and cost effectiveness when compared to other metallic implant materials.

Soumya et al.[2009] has outlined that minuscule cracks and inhomogenous composition of the parts are major hurdles for producing metallic implants via casting and forging. Omar et al.[2012] recently reiterated that metal injection moulding (MIM) that bridges the conventional powder technology and plastic injection moulding is a technique that can provide minimisation of such problems and may contribute to the development of stainless steel implants with higher functionality without increasing the price. MIM that offers combination of near-net shape and cost-effective method of fabricating small-to moderate size metallic implants involves feedstock preparation by mixing metal powder with organic binder, injection moulding, debinding and sintering. Much of the early work on developing binder composition for MIM of SS 316L have been reported [2-10]; however most of them required the use of organic solvents during debinding stage. The binder formulations generally include polyethelene, polypropylene, paraffin wax and stearic acid.

Among many stages in MIM, proper selection of binder is crucial as a feedstock is ussually fragile and brittle due to high metal powder content and lower strength of binders. The selection of binders in MIM is usually based on the aim of producing homogenous feedstock which is free from binder seperation or particle segregation in order to offer high quality injection moulded part. Typically, the binder present in the feedstock acts as a temporary vehicle for shaping the feedstock into required geometry and holding the metal particles in place until the start of the sintering stage. In addition,the most important requisites with regard to the binder are its dimensional stability during debinding, minimum reaction with the metal powder, high green injection moulded strength, good demoulding characteristics, thermal stability and easy and complete removal during debinding [1].

Owing to their biodegradability, starch based binder can be considered as a suitable substitution for synthetic polymer binder in the metal injection moulding (MIM) process. It has been reported that, biodegradable binder is capable to shorten the debinding time and also reduce the injection pressure of the feedstock in the injection moulding process [12]. Starch is suitable to be one of the binder components due to its higher gel strength which consequently leads to formation of harder green injection molded part with lower brittle fracture tendency. In addition, both cassava and rice starch which are locally available and cheap could be utilised as one of the binder components which is safe in practice, environmentally friendly and present fewer hazards to workers and environment during processing of the metal components.

Experimental Procedures

MaterialsThe gas atomised SS 316Lpowder used in this study was obtained from Sandvik Osprey Powder with the average particle size of 14.2 µm. As shown in Figure 1, all the particles were approximately spherical in shape. The sizes of some particles are large, while some are very small. These demonstrated that the powder had a relatively wide particle size distribution which is desirable for efficient particle packing in MIM powder.

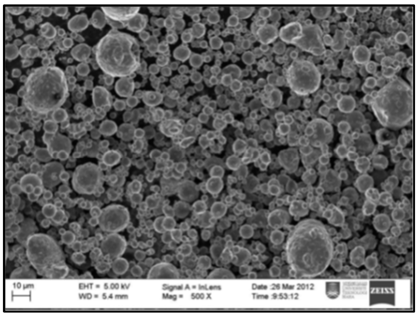


Figure 1:Scanning electron micrograph of 316L Stainless Steel.

Mixing andMoulding The feedstock was prepared by mixing the SS 316Lpowder with a composite binder containing a major fraction of paraffin wax(PW) and starch, which can be removed by two steps solvent debinding, and a minor fraction of polyethelene, that maintains rigidity of the part after leaching of both PW and starch. Two feedstock formulations containing cassava and rice starch at 65 % powder loading were mixed by using a Z-Blade mixer at a temperature of 160ºC for a duration of 2 hours at a speed of 50 rpm to obtain homogeneous paste. Hereafter, these feedstocks are identified as F1 and F2 respectively.The feedstock was then granulated into pallet form so that it could be easily fed into the injection moulding machine.

Table 1: The composition of the feedstock (vol%).

Cassava (CSV) Starch	Rice starch	Paraffin Wax	Polyethylene	Stearic Acid	Feedstock tag
30	-	50	10	10	F1
-	30	50	10	10	F2

The granulated feedstock was molded into tensile bars by using MCP HEK-GMBH vertical injection moulding machine. In order to obtain defect-free molded parts, a suitable set of moulding parameters were established.

Debinding and Sintering The green moulded parts were subjected to a two steps solvent extraction process. Due to solubility of starch in hot water, the first step of solvent debinding was performed by leaching the injection moulded part in water bath at 60^0C for three hours, followed by immersion in a bath of n-heptane at a temperature of 60°C for 2 hours. Upon completion of the solvent extraction process, the brown parts were dried in an oven at a temperature of 47°C for 2 hours to remove the remaining n-heptane. Subsequent thermal pyrolysis was conducted in Lynn furnace. The thermal debinding cycle consists of heating to 450^0C with a heating rate of 3^0C/min, followed by soaking for one hour before furnace cooled.

Sintering was performed at different temperatures between a temperature rangeof 1300°C to 1380°C in vacuum environment. In order to prevent crack formation, the heating rate used was 3°C/min and were soaked for 1 hour and subsequently furnace cooled.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. Microstructure evaluations were performed by optical microscopy and sintered densities were evaluated by Archimedes' method.

Results and Discussions

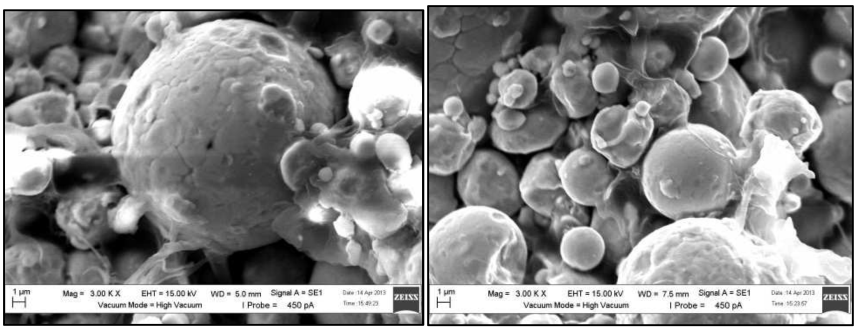
Mixing of the SS 316Lpowder with the multicomponent binder was really easy. Moulding was performed by feeding the granulated feedstock through the vertical metal injection moulding machine into a tensile test specimen. After several trials, both feedstocks were easily moulded at optimum moulding parameters summarized in Table 2. The green injection moulded parts were fairly good and free from normal defects such as short shot, flashes at the parting surface and binder separation.

Table 2: Injection moulding parameters

Injection Pressure(bar)	Nozzle Temperature(^{0}C)	Cycle Time(s)
400	180	18

The green injection moulded parts of F1and F2 exhibit a green density value of 4.80 g/cm^3 and 4.88 g/cm^{3}respectively. The typical density for ferrous based feedstock must be near 5 g/cm^3. This finding (German and Bose, 1997), emphasized that the density of the green injection moulded part is considered to be adequate for MIM parts. It should be clear that, it is always important to achieve sufficient value of green density as the green injection moulded part is subjected to handling prior to debinding and sintering process.This is due to the fact that the feedstock which possessed pseudoplastic behaviour had allowed the moulding pressure to be transmitted uniformly during the injection moulding process, and resulted in better packing of the feedstock into the mold cavity.

The binder present in the injection moulded part provides a mechanical interlocking to the metal powder particles which in turn gives the compact shape and the necessary handling strength required for subsequent processing stages. This is confirmed by micrograph of fracture surface of the injection moulded part shown in Figure 2(a) and (b). It can be clearly seen that the binder components consisting of cassava (CSV) starch/rice starch (RS), paraffin wax (PW), stearic acid (SA), and polyethylene (PE) fill the interstitial sites of SS 316L particles and build a binder network which hold the particles in shape. Further, the micrograph also indicates individual SS 316Lparticles which have been uniformly covered by the binder, thus preventing the SS 316L particles from making a direct surface-to-surface contact.



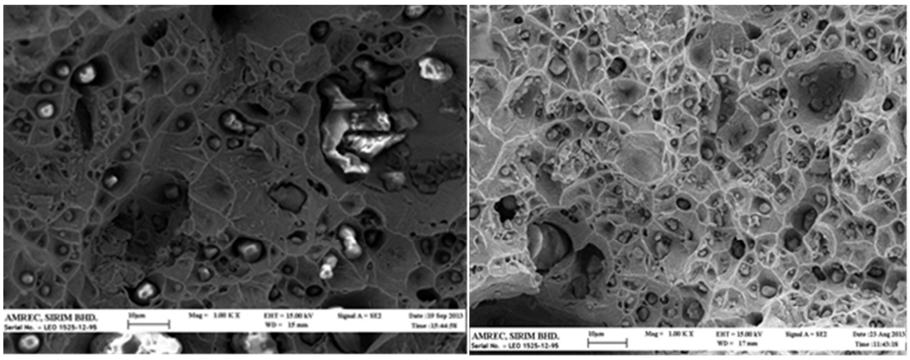
(a) (b)

Figure 2: Scanning electron micrograph of green fractured surface of (a) F1body (b) F2 body

The debinding stage which consumes quite a large amount of time increases the risk of defects formation due to gas produced by evaporation and degrading of the binder components. Solvent debinding technique has been found to be an effective means that allow shortening of debinding time. According to R.M. German (1990), this technique minimise formation of defects such as blistering, cracking and bloating as the binder can be removed from the green part at a slower rate.

For safe and rapid binder removal with minimum possibility of cracks and blister formation, two steps solvent debinding followed by thermal debinding was performed. The water soluble binder component, starch which was removed during the water leaching stage generates pore channels inside the part that allow PW to harmlessly extracted out by means of heptane as a solvent at a temperature of 60^{0}C. The remaining PE functions to hold the SS 316L particles together during and after extracting lower stability binder components to ensure the part had good strength, which was enough to be handled easily.

Figure 3 clearly depicts pore size and pore distribution of the parts which were sintered at 1380^{0}C. In austenitic stainless steel, densification takes place via lattice (volume) diffusion during the intermediate stage sintering and by a combination of grain boundary and lattice diffusion during final stage sintering [10]. Thus, increment in the size of the pores within the grains due Ostwald ripening leads to reduction of the net porosity as a result of the elimination of pores via grain boundary and volume diffusion at high temperatures.



(a) (b)

Figure 3: Scanning electron micrograph of fractured surface of sintered showing pore size and pore distribution in (a) F1 formulation (b) F2 formulation

No defects such as cracks, distortion which might affect the properties were observed in the sintered parts for both binder formulations. The results of physical and mechanical properies of the SS 316L injection moulded part sintered at at a temperature of 1380^{0}C are presented in Table 3.

Table 3: Physical and mechanical properties of SS 316L sintered part

Properties	F1	F2
Density (gm/cm^3)	6.8	8.6
Shrinkage (%)	16.4	18.5
Tensile Strength (Mpa)	229.3	462.1
Hardness (HV)	188.8	385.0

Conclusion

The experimental results obtained in this study indicate thatthemulti-component binder system comprising of paraffin wax (PW), starch, polyethelene(PE)and stearic acid (SA) works successfully with 316L SS powder at maximum injection pressure of 400 bar and a temperature of 180°C. The injection moulded parts for both cassava and rice starch were good and free from normal defects such as short moulding, flashing and parting surfaces. Although the sintered properties of both starch binder formulations comply with the standard ASTM F75, characterization of the sintered parts revealed that rice starch binder formulation possessed properties which are superior compared to cassava starch binder. Hence, rice starch/paraffin wax based formulation has the potential to be a promising biodegradable binder for MIM of SS 316L.

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